

CHAPTER 12 | Thermodynamics: Why Chemical Reactions Happen

12.1. Collect and Organize

From the illustration in Figure P12.1 showing marbles occupying two of the three depressions in a block, we are asked to determine the number of possible arrangements of the marbles before and after the divider is removed.

Analyze

The first block has two red marbles that are indistinguishable from each other, whereas the second block has a red marble and a blue marble. We might expect that the second arrangement might have more possible arrangements because the two marbles are distinguishable.

Solve

- (a) Because the marbles are both red, before the divider is removed there is only one possible arrangement:

| | | |
|---|---|--|
| R | R | |
|---|---|--|

When the divider is removed, there are three possible arrangements:

| | | |
|---|---|--|
| R | R | |
|---|---|--|

| | | |
|---|--|---|
| R | | R |
|---|--|---|

| | | |
|--|---|---|
| | R | R |
|--|---|---|

- (b) When there is one red marble and one blue marble before the divider is removed, there are two possible arrangements:

| | | |
|---|---|--|
| R | B | |
|---|---|--|

| | | |
|---|---|--|
| B | R | |
|---|---|--|

When the divider is removed, there are six possible arrangements:

| | | |
|---|---|--|
| R | B | |
|---|---|--|

| | | |
|---|---|--|
| B | R | |
|---|---|--|

| | | |
|--|---|---|
| | B | R |
|--|---|---|

| | | |
|---|--|---|
| R | | B |
|---|--|---|

| | | |
|--|---|---|
| | R | B |
|--|---|---|

| | | |
|---|--|---|
| B | | R |
|---|--|---|

Think About It

Because there are more possible arrangements for the block with two different marbles, that system has a greater entropy both before and after the divider is removed.

12.2. Collect and Organize

From the illustration in Figure P12.2 showing marbles occupying two of the four depressions in a block, we are asked to determine the number of possible arrangements of the marbles before and after the divider is removed.

Analyze

The first block has two red marbles that are indistinguishable from each other, whereas the second block has a red marble and a blue marble. We might expect that the second arrangement might have more possible arrangements because the two marbles are distinguishable.

Solve

- (a) Because the marbles are both red, before the divider is removed there is only one possible arrangement:

| | | | |
|---|---|--|--|
| R | R | | |
|---|---|--|--|

When the divider is removed, there are six possible arrangements

| | | | |
|---|---|--|--|
| R | R | | |
|---|---|--|--|

| | | | |
|---|--|---|--|
| R | | R | |
|---|--|---|--|

| | | | |
|---|--|--|---|
| R | | | R |
|---|--|--|---|

| | | | |
|--|---|---|--|
| | R | R | |
|--|---|---|--|

| | | | |
|--|---|--|---|
| | R | | R |
|--|---|--|---|

| | | | |
|--|--|---|---|
| | | R | R |
|--|--|---|---|

- (b) Because one marble is red and the other is blue, before the divider is removed there are two possible arrangements:

| | | | |
|---|---|--|--|
| R | B | | |
|---|---|--|--|

| | | | |
|---|---|--|--|
| R | B | | |
|---|---|--|--|

When the divider is removed, there are 12 possible arrangements:

| | | | |
|---|---|--|--|
| R | B | | |
|---|---|--|--|

| | | | |
|---|--|---|--|
| R | | B | |
|---|--|---|--|

| | | | |
|---|--|--|---|
| R | | | B |
|---|--|--|---|

| | | | |
|--|---|---|--|
| | R | B | |
|--|---|---|--|

| | | | |
|--|---|--|---|
| | R | | B |
|--|---|--|---|

| | | | |
|--|--|---|---|
| | | R | B |
|--|--|---|---|

| | | | |
|---|---|--|--|
| B | R | | |
|---|---|--|--|

| | | | |
|---|--|---|--|
| B | | R | |
|---|--|---|--|

| | | | |
|---|--|--|---|
| B | | | R |
|---|--|--|---|

| | | | |
|--|---|---|--|
| | B | R | |
|--|---|---|--|

| | | | |
|--|---|--|---|
| | B | | R |
|--|---|--|---|

| | | | |
|--|--|---|---|
| | | B | R |
|--|--|---|---|

Think About It

Each possible arrangement is a *microstate* for that system. The more microstates, the greater the entropy.

12.3. Collect and Organize

From the illustration in Figure P12.3 of two tires of the same volume inflated at the same temperature but with more air in one than the other, we are to determine which has the greater internal pressure and which has the greater entropy.

Analyze

The tire on the right of Figure P12.3 has more particles of gas in the same volume. As we learned in Chapter 10 in Avogadro's law, pressure is directly proportional to the number of particles in a given volume. Entropy is directly proportional to the number of microstates for a system,

$$S = k \ln W$$

where S is entropy, k is the Boltzmann constant, and W is the number of microstates. A microstate is a unique distribution of particles among energy levels. As the number of particles in a system increases, the number of microstates increases.

Solve

According to Avogadro's law, the tire on the right (with the blue gas), with more gas particles, has the greater internal pressure. For this tire at higher pressure, more microstates are available because of the greater number of gas particles. Therefore, the tire on the right (with the blue gas) also has the greater entropy.

Think About It

When more particles are introduced into a system, the more dispersed the energy is in the system.

12.4. Collect and Organize

For two cubes containing the same quantity of gases, as shown in Figure P12.4, we are to decide which has higher initial entropy and which has higher entropy after sample (a) is cooled and condensed.

Analyze

Cube (a) is larger in volume than cube (b). Entropy, as a measure of the distribution of energy in a system at a specific temperature, is greater for systems with more microstates (particles) and for larger volumes. Also, entropy decreases when a system is cooled because thermal motion decreases for cooled systems, and thus the number of microstates decreases. Furthermore, if a sample of gas condenses to a liquid, it has a significantly lower entropy than when in the gas phase.

Solve

- (a) The larger cube, (a), has more microstates, because it contains more gas particles in a larger volume, and therefore it has greater entropy.
- (b) When sample (a) condenses, its entropy is greatly lowered; sample (b), which remains as a gas, would have more microstates available than sample (a) and hence a greater entropy.

Think About It

For a phase change of a system from vapor to liquid or from liquid to solid, entropy always decreases.

12.5. Collect and Organize

For the system in Figure P12.5, showing a random distribution of two gases, we are to assess the probability that the bottom bulb will collect gas A, which has a molar mass twice that of gas B.

Analyze

The system is already at high entropy because both gases can randomly move throughout the volume.

Solve

For gas A to collect in the bottom bulb of the apparatus, the effect of gravity on the more massive gas particles would have to overwhelm the tendency for gases to be randomly mixed because of entropy. Individual gas molecules are not really affected by gravity, and entropy is the dominant effect. Therefore, atoms of A will not eventually fill the bottom bulb and separate from atoms of B. The probability that gases A and B will separate in the apparatus to occupy separate bulbs is very low. Each gas would in that situation be confined to a smaller volume. That change would involve a decrease in entropy.

Think About It

Gases have enough energy to move anywhere in a container, so the larger the volume the gas occupies, the larger the entropy of the system.

12.6. Collect and Organize

For the change depicted in Figure P12.6, showing a random distribution of two gases in which one of them condenses, we are to assess the change in the entropies of A_2 (red spheres) and B_2 (blue spheres).

Analyze

Gases have higher entropy than liquids, which in turn have higher entropies than solids.

Solve

The figure shows that gas A_2 condenses from the gas phase, whereas gas B_2 remains in the gas phase. Therefore, the entropy of A_2 decreases, whereas that of B_2 remains the same, assuming that the condensation of A_2 did not substantially affect the volume that B_2 can occupy.

Think About It

A larger difference in entropy exists between the gas phase and the liquid phase than between the liquid phase and the solid phase.

12.7. Collect and Organize

For the change depicted in Figure P12.6, we are to consider whether the temperature would be more likely to occur at low or high temperature or would be unaffected by temperature entirely.

Analyze

In the process depicted in Figure P12.6, gas A₂ condenses with a decrease in entropy.

Solve

The change in which A₂ condenses is more likely to occur at low temperatures because at lower temperatures particles have less energy and may condense because of intermolecular forces that overwhelm their energy to remain in the gas phase.

Think About It

From the process shown in Figure P12.6, we can also determine that gas A₂ has a higher boiling point than gas B₂.

12.8. Collect and Organize

From the plot of ΔH and $T\Delta S$ versus temperature in Figure P12.8, we are to consider the significance of the point where the two lines meet and determine over what range of temperature the reaction is spontaneous.

Analyze

Entropy and enthalpy are related by the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

On the plot, ΔH does not change with temperature, but the quantity $T\Delta S$ decreases sharply with an increase in temperature.

Solve

- (a) At the point of intersection, $\Delta H = T\Delta S$, and it is here that $\Delta G = 0$ and the reaction is at equilibrium.
- (b) Because $T\Delta S$ decreases with increasing temperature on the graph, ΔS must be negative. For ΔG to be positive (spontaneous) when $T\Delta S$ is negative, ΔH would have to be less positive (more negative) than $T\Delta S$. That occurs where the ΔH line is below the $T\Delta S$ line, so the reaction is spontaneous below 60°C.

Think About It

If ΔH is positive and $T\Delta S$ is negative (ΔS is negative) for a reaction, according to the Gibbs free energy equation the reaction will never be spontaneous. A plot describing that reaction would have ΔH and $T\Delta S$ lines that never cross.

12.9. Collect and Organize

For the processes of phase changes (melting, vaporization, condensation, freezing, sublimation, and deposition), we are to determine which would have plots of energy versus temperature for ΔH and $T\Delta S$ like that shown in Figure P12.8.

Analyze

As temperature increases, the value of $T\Delta S$ decreases, and so the value of ΔS must be negative.

Solve

Phase changes processes that have $-\Delta S$ are condensation, freezing, and deposition.

Think About It

Those processes are all spontaneous at low temperature. That finding is consistent with our analysis of the plot in Problem 12.8.

12.10. Collect and Organize

Using the representations in Figure P12.10, we are to answer the posed questions.

Analyze

Representations [A], [C], [E], [G], and [I] show gas molecules in different amounts and in different size containers; [E] shows a mixture of two gases. Representation [B] shows frost forming on glass, and [D], [F], and [H] show chemical reactions.

Solve

- (a) When frost forms on window glass, water vapor (the system) is depositing to become solid. The sign of ΔS_{sys} is negative as entropy decreases for the phase change vapor to solid. That would not be spontaneous at high temperature.
- (b) The neutralization reaction between NaHCO_3 and HCl gives off gas as shown in the figure along with the dissolution of the solid NaHCO_3 . Both the production of gas and dissolution increase entropy, so the sign of ΔS_{rxn} is positive.
- (c) For the process of $[\text{D}] \rightarrow [\text{F}]$ a precipitate is formed. We can write any reaction that will give a precipitate. Generically the equation would be $\text{AX}(\text{aq}) + \text{BY}(\text{aq}) \rightarrow \text{AY}(\text{s}) + \text{BX}(\text{aq})$, where A and B are cations and X and Y are anions and the combination of A and Y gives an insoluble salt. One example would be

$$\text{Cd}(\text{NO}_3)_2(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \rightarrow \text{CdS}(\text{s}) + 2\text{NaNO}_3(\text{aq})$$
- (d) When we combine the gases in [A] and [C] to give [E], we are mixing the two gases and each gas will occupy a larger volume. Therefore, the entropy of the system increases.
- (e) When we combine the gases in [G] and [I] to form [E], each gas, although being mixed, will occupy a smaller volume. Therefore, the entropy of the system decreases.
- (f) No, not all mixing will result in an increase in entropy. An increase in entropy due to mixing might be offset by restricting to a smaller volume as in (e) above.

Think About It

Remember that entropy is related to the number of *microstates*. If a substance can occupy more positions or energy states, the greater the entropy.

12.11. Collect and Organize

We consider what happens to the sign of ΔS when we reverse a process.

Analyze

When the sign of ΔS is negative, the process is not favored by entropy, and entropy is decreasing. When the sign of ΔS is positive, the process is favored by entropy, and entropy is increasing.

Solve

If a process favored by entropy ($+\Delta S$) is reversed, the reverse process will not be favored ($-\Delta S$). Therefore, the ΔS when a process is reversed has its sign reversed.

Think About It

In terms of order and disorder in a chemical or physical process, a process that has increasing disorder ($+\Delta S$) has increasing order ($-\Delta S$) when the process is reversed.

12.12. Collect and Organize

For each process described, we are to explain our choice of whether it is spontaneous or nonspontaneous.

Analyze

A spontaneous process is one that, once started, continues without any additional outside intervention.

Solve

- (a) A photovoltaic cell producing electricity is a spontaneous process as long as light is impinging on the surface.
- (b) Dry ice subliming at room temperature is spontaneous because CO_2 gas has greater entropy than solid CO_2 .
- (c) Emission of radiation is spontaneous. Radioactive decay occurs naturally in radioactive elements, and the process continues until all the radioactive elements have been transmuted into nonradioactive elements.

Think About It

Remember that spontaneous reactions are not necessarily fast reactions.

12.13. Collect and Organize

By analyzing the possible outcomes in flipping three coins, we can determine the total number of possible microstates and which of those microstates is most likely.

Analyze

Flipping a coin has two possibilities: heads (H) or tails (T). Because two outcomes are possible for each coin, n coins will have 2^n different possible outcomes. Three coins will have $2^3 = 8$ possibilities.

Solve

The eight possible microstates and their values where $H = +1$ and $T = -1$ are as follows:

| | | | |
|-------|-------------------|-------|-------------------|
| H H H | $(+1 +1 +1) = +3$ | T T T | $(-1 -1 -1) = -3$ |
| H T H | $(+1 -1 +1) = +1$ | T H T | $(-1 +1 -1) = -1$ |
| H H T | $(+1 +1 -1) = +1$ | T T H | $(-1 -1 +1) = -1$ |
| T H H | $(-1 +1 +1) = +1$ | H T T | $(+1 -1 -1) = -1$ |

The most likely microstates have sums of $+1$ and -1 .

Think About It

As the number of coins increases, the number of possible microstates increases significantly. For $n = 4$, there are 16 possibilities, for $n = 5$ there are 32, and for $n = 6$ there are 64.

12.14. Collect and Organize

By analyzing the possible outcomes in arranging four chairs on four steps, we can determine the total number of microstates possible for the chairs when we can distinguish them from each other because they have different numbers on their backs.

Analyze

Each chair has the possibility of being on any of the steps, but no two chairs can be on the same step. Therefore, the placement of the second and later chairs on the steps is not independent of where another chair has already been placed.

Solve

Because four outcomes are possible for placement of the first chair but that placement of the first chair restricts the placement of the second chair, which restricts the placement of the third chair and then the placement of the fourth chair, the number of possible outcomes is $4!$, or $4 \times 3 \times 2 \times 1$.

The 24 possible microstates for the chairs on four different steps are as follows:

| | | | |
|------|------|------|------|
| 1234 | 2341 | 3412 | 4123 |
| 1342 | 2314 | 3421 | 4132 |
| 1423 | 2431 | 3142 | 4231 |
| 1432 | 2413 | 3124 | 4213 |
| 1324 | 2134 | 3214 | 4312 |
| 1243 | 2143 | 3241 | 4321 |

Think About It

In this situation, no one set of chair placements is more likely than another.

12.15. Collect and Organize

From the standard molar entropy value of liquid water at 298 K, we are to calculate the number of microstates available to a single molecule of H_2O .

Analyze

The value of S° for $H_2O(l)$ from Appendix 4 is $69.9 \text{ J/mol} \cdot \text{K}$, and the equation relating the molar entropy to the number of possible microstates is

$$S = k_B \ln W$$

where S is the entropy of the system under consideration, k_B is the Boltzmann constant (1.382×10^{-23} J/K), and W is the number of microstates possible.

Solve

We must rearrange the equation to solve for W and use Avogadro's number to determine the possible microstates for just one molecule of liquid water, not an entire mole of liquid water molecules.

$$W = e^{S/k_B}$$

$$\text{where } S/k_B = \frac{\left(69.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \left(\frac{1 \text{ mol}}{6.0221 \times 10^{23} \text{ molecules}}\right)}{1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}} = 8.405$$

$$W = e^{8.405} = 4.47 \times 10^3$$

Think About It

For an entire mole of water molecules,

$$W = e^{S/k_B}$$

$$\text{where } S/k_B = \frac{\left(69.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)}{1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}} = 5.06 \times 10^{24}$$

$$W = e^{5.06 \times 10^{24}} \text{ is beyond the capabilities of most scientific calculators.}$$

12.16. Collect and Organize

From the standard molar entropy value of gaseous nitrogen, 298 K, we are to calculate the number of microstates available to a single molecule of N_2 .

Analyze

The value of S° for $\text{N}_2\text{O(g)}$ from Appendix 4 is $191.5 \text{ J/mol} \cdot \text{K}$, and the equation relating the molar entropy to the number of possible microstates is

$$S = k_B \ln W$$

where S is the entropy of the system under consideration, k_B is the Boltzmann constant (1.382×10^{-23} J/K), and W is the number of microstates possible.

Solve

We must rearrange the equation to solve for W and use Avogadro's number to determine the possible microstates for just one molecule of nitrogen, not an entire mole of nitrogen molecules.

$$W = e^{S/k_B}$$

$$\text{where } S/k_B = \frac{\left(191.5 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \left(\frac{1 \text{ mol}}{6.0221 \times 10^{23} \text{ molecules}}\right)}{1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}} = 23.0265$$

$$W = e^{23.0265} = 1.001 \times 10^{10}$$

Think About It

The higher the entropy of a system, the more possible microstates.

12.17. Collect and Organize

For the three containers shown in Figure P12.17, each containing five gaseous particles, we are to rank them in order of the increasing number of microstates for the molecules in the containers.

Analyze

The higher the entropy of the system, the more possible microstates for the system. All the substances are gases, so no difference in the entropy due to difference in phase is present. What is different is the number of atoms in the five molecules in each container. Using the atomic color palette in the textbook, we can even assign those molecules (where red = oxygen and blue = nitrogen) as (a) NO_2 , (b) O_2 , and (c) N_2O_2 .

Solve

The larger the molecules, the greater the entropy because a larger molecule with more atoms has more rotational energy levels, so they have more accessible microstates. Of those three gases, (c) is the largest and (b) is the smallest. In order of increasing number of accessible microstates: (b) < (a) < (c).

Think About It

We expect, too, that the molar entropies would increase in the same order: (b) O_2 ($205.0 \text{ J/mol} \cdot \text{K}$) < (a) NO_2 ($240 \text{ J/mol} \cdot \text{K}$) < (c) N_2O_2 (unstable, so no value found).

12.18. Collect and Organize

For the two cylinders shown in Figure P12.18, each containing the same number of gaseous particles (9), we are to compare the number of microstates available to the molecules in a small volume versus a larger volume.

Analyze

The higher the entropy of the system, the more possible microstates for the system. The greater the volume in which gaseous particles can move, the greater the entropy and the more microstates accessible to the system.

Solve

The larger-volume cylinder (b) has more accessible microstates.

Think About It

More microstates would also be accessible to the system if we did not change the volume but increased the number of gaseous molecules present in the system.

12.19. Collect and Organize

Given five ionic solutes, we are to predict which experiences the greatest increase in entropy when 0.0100 mol of the substance dissolves in 1 L of water.

Analyze

All those substances are ionic substances and, when dissolved in water, separate into the constituent cations and anions. Therefore, each will experience an increase in entropy upon dissolution. However, the one that produces the most dissolved ions will experience the greatest increase in entropy when dissolved into the same volume of water at the same initial concentration of the ionic salt.

Solve

- (a) CaCl_2 dissolves into one Ca^{2+} cation and two Cl^- anions in solution, giving a total of three dissolved ions.
 - (b) NaBr dissolves into one Na^+ cation and one Br^- anion in solution, giving a total of two dissolved ions.
 - (c) KCl dissolves into one K^+ cation and one Cl^- anion in solution, giving a total of two dissolved ions.
 - (d) $\text{Cr}(\text{NO}_3)_3$ dissolves into one Cr^{3+} cation and three NO_3^- anions in solution, giving a total of four dissolved ions.
 - (e) LiOH dissolves into one Li^+ cation and one OH^- anion in solution, giving a total of two dissolved ions.
- Because (d) $\text{Cr}(\text{NO}_3)_3$ yields the most dissolved ions, it is the salt that experiences the greatest increase in entropy upon dissolution.

Think About It

The total concentration of dissolved ions (both cation and anion) for the $\text{Cr}(\text{NO}_3)_3$ solution is 0.0400 M .

12.20. Collect and Organize

Given five molecular solutes, we are to predict which experiences the greatest increase in entropy upon dissolution in water.

Analyze

Some of the molecular substances are gases (HF and CO₂) and others are liquids (CH₃OH and CH₃COOH) or solids (C₁₂H₂₂O₁₁). Gases have a significantly higher entropy than liquids, which in turn have a higher entropy than solids. When substances dissolve in water, they are entering the liquid phase from their original phase.

Solve

Dissolving a high-entropy gas into water would result in a decrease in entropy because the liquid phase is lower in entropy than the gaseous phase. Therefore, (a) CO₂ and (b) HF do not experience an increase in entropy upon dissolution. However, (c) CH₃OH and (d) CH₃COOH, as liquids being dispersed into another liquid, are experiencing an increase in entropy upon dissolution, as is (e) C₁₂H₂₂O₁₁, as molecules in the solid lattice of the crystal are being dispersed in the water. Therefore, (c), (d), and (e) have an increase in entropy upon dissolution in water.

Think About It

We might predict that the entropy increase for the dissolution of a solid in water might often be greater than the dissolution of a liquid in water because most solids have lower molar entropies than most liquids.

12.21. Collect and Organize

Given pairs of systems, we are asked to determine which of the pair has the greater entropy.

Analyze

The system with the most accessible microstates will have greater entropy. Systems that have larger molecules (with the particles being in the same phase) will have greater entropy. Gases have significantly greater entropy than either liquids or solids. Systems that have more particles (with the particles in the same phase) have greater entropy.

Solve

- (a) Both S₈(g) and S₂(g) are present in the same number of particles and in the same phase. S₈(g) has greater entropy because it is a larger molecule than S₂(g).
- (b) Both S₈(s) and S₂(g) are present in the same number of particles but are present in different phases. S₂(g) has greater entropy because it is in the gas phase, compared with the entropy of S₈ in the solid phase.
- (c) Both O₂(g) and O₃(g) are present in the same number of particles and in the same phase. O₃(g) has greater entropy because it is a larger molecule than O₂(g).

Think About It

For the same mass of gaseous S₈ and S₂, S₂ would have the greater entropy, as it would have more particles present because of its lower molar mass.

12.22. Collect and Organize

For the process of a pharmaceutical adding a sugar molecule during metabolism, we are to predict whether the process increases or decreases entropy.

Analyze

More complex structures have lower entropy than those that are simple.

Solve

Adding a molecule of sugar to the drug morphine, as shown in Figure P12.22, results in a more complex structure. Therefore, the entropy of the system of that process decreases.

Think About It

As we will see, decreasing entropy is not favorable, but it is possible when the overall entropy of the universe increases for that process.

12.23. Collect and Organize

We are to predict which has the higher standard molar entropy, diamond or the fullerenes.

Analyze

Diamond is a three-dimensional, highly ordered network of covalently bonded carbon atoms. Fullerenes are also made up of covalently bonded carbon atoms, but they form discrete structures instead of an extended network.

Solve

Fullerenes, with less extensive bonding, have a higher standard molar entropy than diamond.

Think About It

We would expect the standard molar entropy of graphite to be between that of diamond and the fullerenes because of its intermediate structure.

12.24. Collect and Organize

For the conversion of liquid ^3He into its superfluid state, showing frictionless flow and known to be ordered, we are to predict the sign of the entropy change.

Analyze

Liquids have more entropy than the more ordered solid state. From the statement of the problem, we know that ^3He is converting into a more ordered form of liquid ^3He .

Solve

If the $^3\text{He}(\ell)$ is becoming more ordered to reach superfluidity, the sign of the entropy change must be negative.

Think About It

For superfluids, the viscosity is zero; those fluids show no resistance to flow.

12.25. Collect and Organize

By considering the phase and size of a compound, we can rank the compounds in each series in order of increasing standard molar entropy.

Analyze

In general, compounds in the same phase that are larger have greater S° .

Solve

- (a) $\text{CH}_4(\text{g}) < \text{CF}_4(\text{g}) < \text{CCl}_4(\text{g})$
- (b) $\text{CH}_2\text{O}(\text{g}) < \text{CH}_3\text{CHO}(\text{g}) < \text{CH}_3\text{CH}_2\text{CHO}(\text{g})$
- (c) $\text{HF}(\text{g}) < \text{H}_2\text{O}(\text{g}) < \text{NH}_3(\text{g})$

Think About It

Larger molecules have greater S° because they have more opportunities for internal and rotational motion.

12.26. Collect and Organize

By considering the phase and size of a compound, we can rank the compounds in each series in order of increasing standard molar entropy.

Analyze

In general, gaseous compounds of roughly equal size have a higher S° than liquids. Also, larger compounds have greater S° .

Solve

- (a) $\text{CH}_4(\text{g}) < \text{CH}_3\text{CH}_3(\text{g}) < \text{CH}_3\text{CH}_2\text{CH}_3(\text{g})$ because the sizes of the molecules increase.
- (b) $\text{CH}_2\text{Cl}_2(\ell) < \text{CHCl}_3(\ell) < \text{CCl}_4(\ell)$ because the sizes of the molecules increase.
- (c) $\text{CO}_2(\ell) < \text{CO}_2(\text{g}) < \text{CS}_2(\text{g})$ because the gaseous form of CO_2 has greater S° than the liquid form and $\text{CS}_2(\text{g})$ is a larger molecule than $\text{CO}_2(\text{g})$.

Think About It

Larger molecules have greater S° because they have more opportunities for internal and rotational motion.

12.27. Collect and Organize

Given ice cubes (the system) in a glass of lemonade (the surroundings), we are to determine the signs of ΔS for the system and for the surroundings as the ice cools the lemonade from 10.0°C to 0.0°C.

Analyze

Cooling is the result of decreased molecular motion, which is correlated to a decrease in entropy.

Solve

The sign of ΔS_{surr} is negative because the lemonade is cooling, which decreases the motion of the lemonade molecules. The sign of ΔS_{sys} is positive because the ice is melting. When a phase change from solid to liquid occurs in the lemonade, disorder, and therefore entropy of the substance, increases.

Think About It

Here, as long as $\Delta S_{\text{sys}} > -\Delta S_{\text{surr}}$, the process is spontaneous.

12.28. Collect and Organize

Given that the temperature of water (the surroundings) increases when CaCl_2 (the system) is dissolved in it, we are to determine the signs of ΔS for the system and for the surroundings as the calcium chloride dissolves.

Analyze

Heating is the result of increased molecular motion, which is correlated to an increase in entropy.

Solve

The sign of ΔS_{surr} is positive because the water is warming, which increases the motion of the water molecules. The sign of ΔS_{sys} is positive because the salt is dissolving, forming three ions (1 Ca^{2+} and 2 Cl^-) in solution.

Think About It

Here, both ΔS_{sys} and ΔS_{surr} are positive, so ΔS_{univ} is increasing and the process is spontaneous.

12.29. Collect and Organize

Given three combinations of signs for changes in entropy for the system, the surroundings, and the universe, we are to determine which combinations are possible.

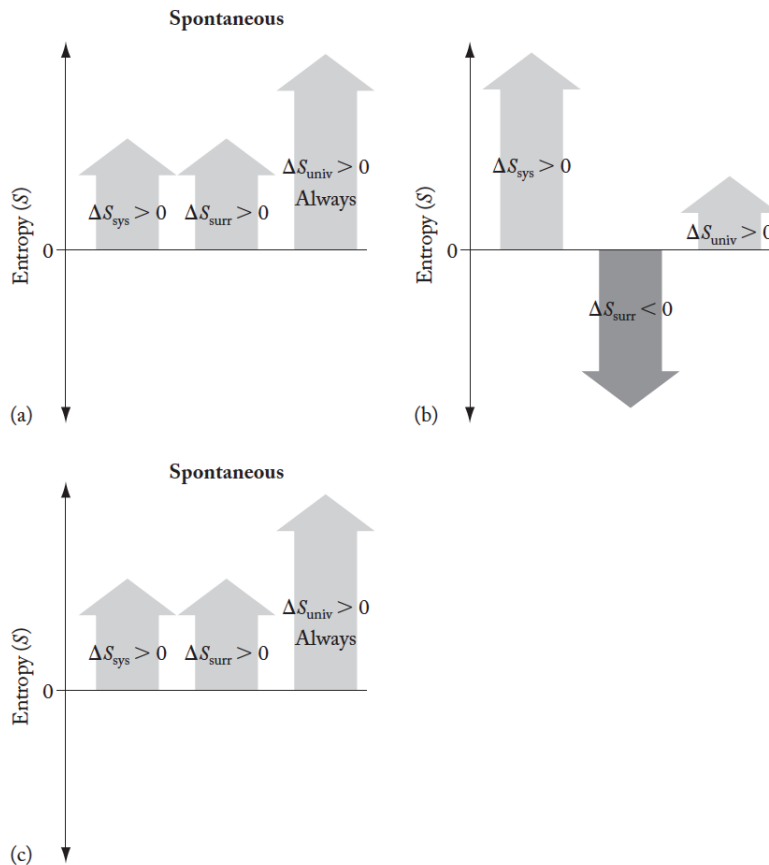
Analyze

For a process to occur, the second law of thermodynamics must be obeyed. That law states that the combination of the change in entropy for a system and the change in entropy for the surroundings must be equal to the change in entropy for the universe. Therefore, ΔS_{univ} , which is equal to $\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$, must be greater than zero for a process to occur and

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Solve

- (a) If $\Delta S_{\text{sys}} > 0$ and $\Delta S_{\text{surr}} > 0$, then $\Delta S_{\text{univ}} > 0$ for all ΔS_{surr} and ΔS_{sys} . That combination of entropy changes is always possible.
- (b) If $\Delta S_{\text{sys}} > 0$ and $\Delta S_{\text{surr}} < 0$, then $\Delta S_{\text{univ}} > 0$ when $\Delta S_{\text{sys}} > -\Delta S_{\text{surr}}$. That combination of entropy changes is possible.
- (c) If $\Delta S_{\text{sys}} > 0$ and $\Delta S_{\text{surr}} > 0$, then ΔS_{univ} must be > 0 for all ΔS_{surr} and ΔS_{sys} . Therefore, ΔS_{univ} cannot be < 0 for those changes in entropy for the system and the surroundings, so that combination of entropy changes is not possible.

**Think About It**

In part c, ΔS_{univ} would be calculated as <0 if ΔS_{sys} and ΔS_{surr} were both <0 or if $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} < 0$. That process, however, would not be spontaneous.

12.30. Collect and Organize

For three combinations of ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} , we are to determine which are mathematically possible for a process.

Analyze

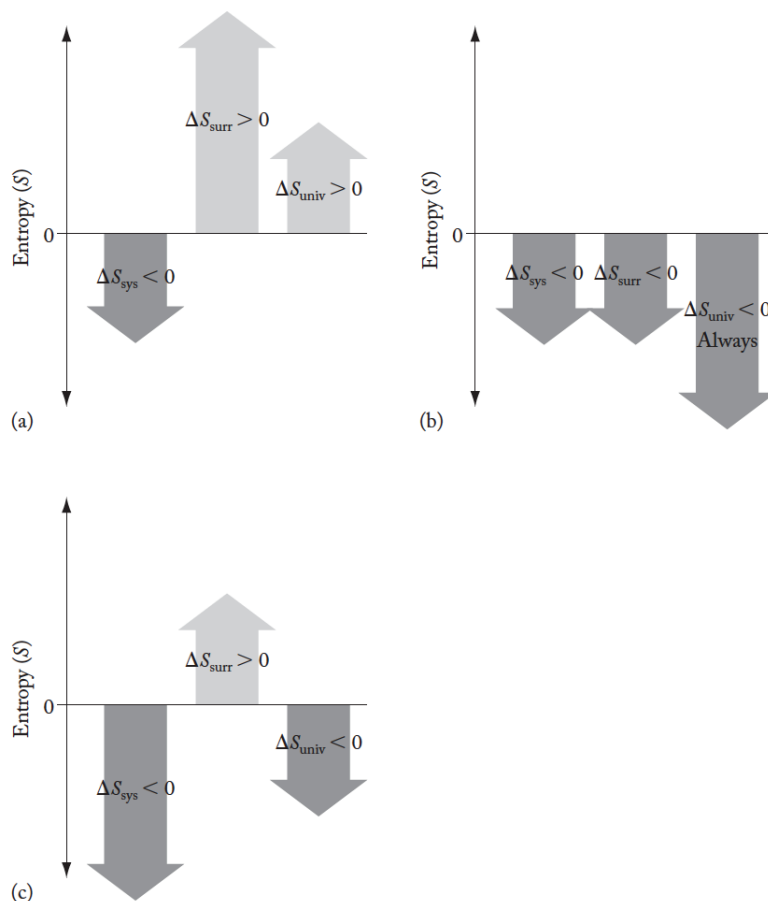
For spontaneous processes,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

The change in entropy for any spontaneous process must always result in $\Delta S_{\text{univ}} > 0$.

Solve

- When $\Delta S_{\text{sys}} < 0$, and $\Delta S_{\text{surr}} > 0$, it is possible for ΔS_{univ} to be > 0 as long as ΔS_{surr} is more positive than ΔS_{sys} is negative.
- When $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{surr}} < 0$, it is not possible for ΔS_{univ} to be > 0 because the sum of two negative values gives $\Delta S_{\text{univ}} < 0$.
- When $\Delta S_{\text{sys}} < 0$ and $\Delta S_{\text{surr}} > 0$, it is possible for ΔS_{univ} to be < 0 as long as ΔS_{sys} is more negative than ΔS_{surr} is positive.

**Think About It**

From that analysis, we realize that we may have a spontaneous process that becomes more ordered in the system, as long as a more positive entropy change occurs for the surroundings.

12.31. Collect and Organize

For the reaction of H_2S with O_2 to form S_8 and H_2O , we are asked to predict whether the change in entropy for the system increases or decreases.

Analyze

Both reactants and one product are gases in this reaction, but sulfur (S_8) is produced as a solid. Entropy for gases is much greater than that for solids.

Solve

Because there are 9 moles of gas as reactants and only 2 moles of gas and 3 moles of solid (with much lower entropy) as products, the number of gaseous, high-entropy species decreases for the reaction. Therefore, the entropy of the system decreases.

Think About It

That does not predict that the reaction is not spontaneous, however. We must also examine the change in entropy of the universe; if $\Delta S_{\text{univ}} > 0$, the reaction will theoretically proceed.

12.32. Collect and Organize

For the reaction of NaCl with H_2O to form NaOH , H_2 , and Cl_2 , we are asked to predict whether the change in entropy for the system increases or decreases.

Analyze

Both reactants and one product are either in solution or are pure liquids, whereas H_2 and Cl_2 are produced as gases. Entropy for gases is much greater than that for either solutions or liquids.

Solve

Because two moles of high-entropy gas are produced in that reaction from reactants in solution or as liquids, the entropy of the system increases.

Think About It

That does not predict that the reaction is spontaneous, however. We must also examine the change in entropy of the universe; if $\Delta S_{\text{univ}} > \Delta S_{\text{sys}}$, the reaction will theoretically proceed.

12.33. Collect and Organize

Given that a chemical reaction has $\Delta S_{\text{sys}} = -66.0 \text{ J/K}$, we are to determine the value of ΔS_{surr} needed for the reaction to be nonspontaneous.

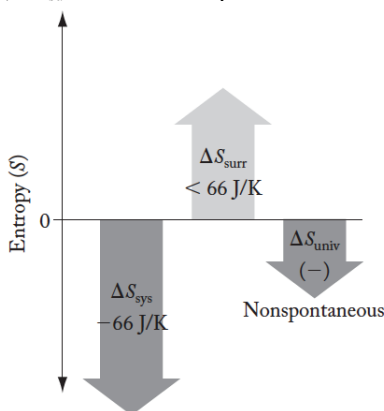
Analyze

For a nonspontaneous process,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} < 0$$

Solve

For the reaction to be nonspontaneous, ΔS_{surr} must be less positive than $+66.0 \text{ J/K}$.

**Think About It**

If ΔS_{surr} is more positive than 66.0 J/K , then $\Delta S_{\text{univ}} > 0$ and the reaction would be spontaneous.

12.34. Collect and Organize

Given that a chemical reaction has $\Delta S_{\text{sys}} = 72.0 \text{ J/K}$, we are to determine the value of ΔS_{surr} in order that the reaction be spontaneous.

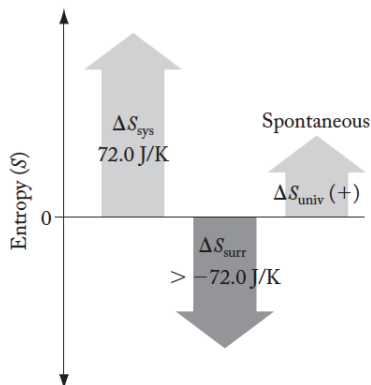
Analyze

For a spontaneous process,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Solve

For the reaction to be spontaneous, ΔS_{surr} must be greater (more positive) than -72.0 J/K .

**Think About It**

If ΔS_{surr} were more negative than -72.0 J/K , then $\Delta S_{\text{univ}} < 0$ and the reaction would be nonspontaneous.

12.35. Collect and Organize

When the products of a process have a greater entropy (more positive) than the reactants, we are to determine the sign of the entropy change for the overall process, $\Delta S_{\text{rxn}}^{\circ}$.

Analyze

The entropy change for a process is calculated from

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_{\text{products}} S_{\text{products}}^{\circ} - \sum n_{\text{reactants}} S_{\text{reactants}}^{\circ}$$

Solve

If $nS_{\text{products}}^{\circ} > mS_{\text{reactants}}^{\circ}$, then $\Delta S_{\text{rxn}}^{\circ}$ for the process is positive.

Think About It

A positive $\Delta S_{\text{rxn}}^{\circ}$ means that the process resulted in more energy dispersal in the reaction.

12.36. Collect and Organize

We are asked to predict the sign of $\Delta S_{\text{rxn}}^{\circ}$ for decomposition reactions and explain our choice.

Analyze

Decomposition reactions involve the breakup of a substance into constituent parts.

Solve

The sign of $\Delta S_{\text{rxn}}^{\circ}$ will be positive (greater than zero) because in decomposition reactions a substance is broken down into smaller parts, meaning that more particles are produced.

Think About It

If any heat is given off in the decomposition reaction that is transferred to the surroundings, the sign of ΔS_{surr} for the decomposition reaction will be positive.

12.37. Collect and Organize

We are asked to predict the sign of $\Delta S_{\text{rxn}}^{\circ}$ for precipitation reactions and explain our choice.

Analyze

Precipitation reactions involve the formation of a solid from dispersed ionic or molecular solutes in a solution.

Solve

The sign of $\Delta S_{\text{rxn}}^{\circ}$ will be negative (less than zero) because in precipitation reactions solid products will have a lower molar entropy than the dispersed ions or molecules in the solution from which the precipitate forms.

Think About It

Precipitation reactions may be endothermic or exothermic, so the ΔS_{surr} may be either negative or positive.

12.38. Collect and Organize

We are asked to predict the sign of ΔS for the given reactions.

Analyze

When the products of a process have a greater entropy (more positive) than the reactants, then sign of entropy for the process is positive. The entropy of a solid is lower (less positive) than the entropy of a liquid which, in turn, is lower than the entropy of a gas. If more moles of gaseous products are formed in a reaction than moles of gaseous reactants, entropy of the system is increasing (becoming more positive).

Solve

- (a) ΔS is negative because a gaseous reactant (Cl_2) reacts to form a solid (NaCl).
- (b) ΔS is positive because the reaction forms a gaseous product (PH_3) from a liquid reactant.
- (c) ΔS cannot be judged because no change occurs in the number of moles of gas in going from reactants to products and the reactants and products have similar molecular complexity (one reactant and product is diatomic and the other reactant and product are triatomic).
- (d) ΔS cannot be judged because no change occurs in the number of moles of gas in going from reactants to products and the two solids are of similar molecular complexity.

Think About It

It is unlikely that ΔS_{rxn} for (c) and (d) are zero; we can use tabulated values and the equation

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_{\text{products}} S_{\text{products}}^{\circ} - \sum n_{\text{reactants}} S_{\text{reactants}}^{\circ}$$

to calculate the ΔS_{rxn} for those reactions.

12.39. Collect and Organize

Using values of S° for the reactants and products for four atmospheric reactions, we are to calculate $\Delta S_{\text{rxn}}^{\circ}$. Standard molar entropies are in Appendix 4.

Analyze

A change in entropy for a reaction is

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_{\text{products}} S_{\text{products}}^{\circ} - \sum n_{\text{reactants}} S_{\text{reactants}}^{\circ}$$

Solve

- (a) $\Delta S_{\text{rxn}}^{\circ} = (2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K})$
 $- [(1 \text{ mol N}_2 \times 191.5 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K})]$
 $= 24.9 \text{ J/K}$
- (b) $\Delta S_{\text{rxn}}^{\circ} = (2 \text{ mol NO}_2 \times 240.0 \text{ J/mol} \cdot \text{K})$
 $- [(2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K})]$
 $= -146.4 \text{ J/K}$
- (c) $\Delta S_{\text{rxn}}^{\circ} = (1 \text{ mol NO}_2 \times 240.0 \text{ J/mol} \cdot \text{K})$
 $- [(1 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) + (\frac{1}{2} \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K})]$
 $= -73.2 \text{ J/K}$
- (d) $\Delta S_{\text{rxn}}^{\circ} = (1 \text{ mol N}_2\text{O}_4 \times 304.2 \text{ J/mol} \cdot \text{K}) - (2 \text{ mol NO}_2 \times 240.0 \text{ J/mol} \cdot \text{K})$
 $= -175.8 \text{ J/K}$

Think About It

Because the balanced equation in part b is twice that in part c, the value of the entropy change for the reaction is doubled.

12.40. Collect and Organize

For each reaction, we can use S° values for the products and reactants found in Appendix 4 to compute $\Delta S^\circ_{\text{rxn}}$.

Analyze

The entropy of change for a reaction is given by

$$\Delta S^\circ_{\text{rxn}} = \sum n_{\text{products}} S^\circ_{\text{products}} - \sum n_{\text{reactants}} S^\circ_{\text{reactants}}$$

Solve

$$\begin{aligned} \text{(a)} \quad \Delta S^\circ_{\text{rxn}} &= \left[(1 \text{ mol SO}_2 \times 248.2 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol H}_2\text{S} \times 205.6 \text{ J/mol} \cdot \text{K}) + \left(\frac{3}{2} \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K} \right) \right] \\ &= -76.1 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta S^\circ_{\text{rxn}} &= (2 \text{ mol SO}_3 \times 256.8 \text{ J/mol} \cdot \text{K}) \\ &\quad - \left[(2 \text{ mol SO}_2 \times 248.2 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\ &= -187.8 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta S^\circ_{\text{rxn}} &= (1 \text{ mol H}_2\text{SO}_4 \times 20.1 \text{ J/mol} \cdot \text{K}) \\ &\quad - \left[(1 \text{ mol SO}_3 \times 256.8 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol H}_2\text{O} \times 69.9 \text{ J/mol} \cdot \text{K}) \right] \\ &= -306.6 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \text{(d)} \quad \Delta S^\circ_{\text{rxn}} &= (1 \text{ mol SO}_2 \times 248.2 \text{ J/mol} \cdot \text{K}) \\ &\quad - \left[(1 \text{ mol S} \times 167.8 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\ &= -124.6 \text{ J/K} \end{aligned}$$

Think About It

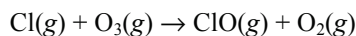
The signs of $\Delta S^\circ_{\text{rxn}}$ for those reactions are what would be expected considering that when the number of independently moving molecules in a reaction decreases in going from reactants to products, the entropy of the system decreases.

12.41. Collect and Organize

Given the $\Delta S^\circ_{\text{rxn}}$ for the conversion of Cl and O₃ into ClO and O₂ and the S° for Cl, O₃, and O₂ from Appendix 4, we are to calculate S° for ClO.

Analyze

To calculate $\Delta S^\circ_{\text{rxn}}$ we need $S^\circ_{\text{O}_3} = 238.8 \text{ J/mol} \cdot \text{K}$, $S^\circ_{\text{Cl}} = 165.2 \text{ J/mol} \cdot \text{K}$, and $S^\circ_{\text{O}_2} = 205.0 \text{ J/mol} \cdot \text{K}$ along with the balanced equation



The change in entropy for a reaction is

$$\Delta S^\circ_{\text{rxn}} = \sum n_{\text{products}} S^\circ_{\text{products}} - \sum n_{\text{reactants}} S^\circ_{\text{reactants}}$$

Solve

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= 19.9 \text{ J/K} = \left[(1 \text{ mol ClO} \times S^\circ_{\text{ClO}}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol Cl} \times 165.2 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_3 \times 238.8 \text{ J/mol} \cdot \text{K}) \right] \end{aligned}$$

$$19.9 \text{ J/K} = -199.0 \text{ J/K} + S_{\text{ClO}}^{\circ}$$

$$S_{\text{ClO}}^{\circ} = 218.9 \text{ J/mol} \cdot \text{K}$$

Think About It

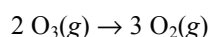
Because $\Delta S_{\text{rxn}}^{\circ}$ is positive, the entropy for the system (the reaction) increases when Cl and O₃ react to form ClO and O₂.

12.42. Collect and Organize

We are to calculate ΔS° for the conversion of O₃ to O₂ and compare its entropy with the ΔS° for the same conversion, but with Cl atoms involved in the reaction in Problem 12.41.

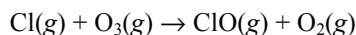
Analyze

To calculate $\Delta S_{\text{rxn}}^{\circ}$, we need $S_{\text{O}_3}^{\circ} = 238.8 \text{ J/mol} \cdot \text{K}$ and $S_{\text{O}_2}^{\circ} = 205.0 \text{ J/mol} \cdot \text{K}$ along with the balanced equation

**Solve**

$$\begin{aligned} \Delta S_{\text{rxn}}^{\circ} (\text{without Cl}) &= (3 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) - (2 \text{ mol O}_3 \times 238.8 \text{ J/mol} \cdot \text{K}) \\ &= 137.4 \text{ J/K} \end{aligned}$$

That is for the decomposition of 2 mol of O₃. For 1 mol of O₃, ΔS° would be $137.4 \text{ J/K} \div 2 = 68.7 \text{ J/K}$. In comparing that value with 19.9 J/K for the conversion of O₃ to O₂ in the presence of Cl atoms,



we see that the entropy change is more positive for that reaction without Cl.

Think About It

That answer makes sense because when Cl is present, the entropy associated with forming the Cl—O bond is negative.

12.43. Collect and Organize

We are to explain what the sign of ΔG tells us about the spontaneity of a reaction.

Analyze

Free energy is related to the entropy change of the universe by

$$\Delta G_{\text{sys}} = -T \Delta S_{\text{univ}}$$

Solve

When ΔS_{univ} is positive, the process is spontaneous, so for spontaneous processes according to the equation

$$\Delta G_{\text{sys}} = -T \Delta S_{\text{univ}}$$

ΔG_{sys} is negative. Likewise, for a nonspontaneous process, ΔG_{sys} is positive.

Think About It

A negative free energy change for a reaction means that the free energy at the end of the process is lower than at the beginning of the process.

12.44. Collect and Organize

We are to explain what the sign of ΔG tells us about the rate of a reaction.

Analyze

Free energy is related to the entropy change of the universe by

$$\Delta G_{\text{sys}} = -T \Delta S_{\text{univ}}$$

and is relevant to the change in free energy at the end of a reaction compared with the free energy at the beginning of that reaction.

Solve

Because a change in free energy for a reaction is only a comparison of the final and initial energy states of the process, the sign of ΔG tells us nothing about the rate at which that reaction occurs.

Think About It

A reaction could indeed be spontaneous (such as the conversion of diamond to graphite) but be very slow.

12.45. Collect and Organize

We are to explain why 19th-century scientists believed that all exothermic reactions were spontaneous.

Analyze

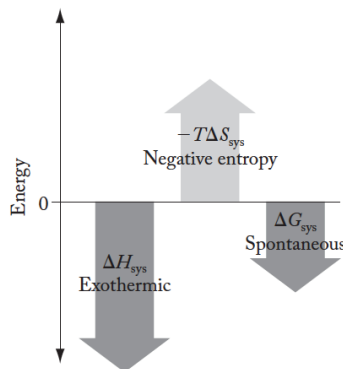
A reaction is spontaneous when its free-energy change is negative according to the equation

$$\Delta G = \Delta H - T\Delta S$$

When H is negative, the reaction is exothermic.

Solve

The enthalpy of reactions is usually on the order of kilojoules per mole, whereas the entropy change for reactions is usually on the joules-per-mole scale. Therefore, many exothermic reactions are spontaneous because the magnitude of ΔH is greater than the magnitude of ΔS , so ΔG is usually negative, indicating a spontaneous reaction when the reaction is exothermic ($-\Delta H$).

**Think About It**

The assumption that all exothermic reactions are spontaneous, though, is incorrect. If the value of $T\Delta S$ is more negative than the value of H , then ΔG would be positive and the reaction would be nonspontaneous.

12.46. Collect and Organize

Given the signs of ΔG_{rxn} , we are asked to determine in which way each reaction will proceed.

Analyze

When $\Delta G_{\text{rxn}} < 0$ (negative), the reaction is spontaneous as written from left to right. When $\Delta G_{\text{rxn}} > 0$ (positive), the reaction is nonspontaneous as written from left to right but is spontaneous as written from right to left (the reverse reaction). When $\Delta G_{\text{rxn}} = 0$, the reaction is at equilibrium, and neither the forward nor the reverse reaction is spontaneous.

Solve

- (a) When $\Delta G_{\text{rxn}} < 0$ (negative), the reaction will proceed to the right, toward products.
- (b) When $\Delta G_{\text{rxn}} = 0$, the reaction will not proceed either toward products or toward reactants.
- (c) When $\Delta G_{\text{rxn}} > 0$ (positive), the reaction will proceed to the left, toward reactants.

Think About It

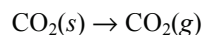
When a reaction is at equilibrium, neither the concentration of the reactants nor that of the products changes.

12.47. Collect and Organize

For the sublimation of dry ice at room temperature, we are to determine the signs of ΔS , ΔH , and ΔG .

Analyze

The reaction describing the sublimation is

**Solve**

ΔS is positive because the solid is subliming to a gas, which has much greater entropy.

ΔH is positive because heat is required to effect the phase change.

ΔG is negative because at room temperature (25°C) sublimation occurs spontaneously.

Think About It

The spontaneity of that process depends on temperature. At lower temperatures the value of $T\Delta S$ in the equation

$$\Delta G = \Delta H - T\Delta S$$

would not be great enough to give a negative value for ΔG .

12.48. Collect and Organize

For dew forming on a cool night, we are to determine the sign (negative or positive) of ΔS , ΔH , and ΔG .

Analyze

When entropy is increasing, ΔS is positive; when entropy is decreasing, ΔS is negative. An exothermic process has a negative ΔH ; an endothermic process has a positive ΔH . A spontaneous process has a negative ΔG ; a nonspontaneous process has a positive ΔG .

Solve

Because dew is formed through the condensation of gaseous water into liquid water and liquid water has lower entropy than water vapor, ΔS is negative. The process is exothermic, so ΔH is negative (it is exothermic because the reverse process of liquid \rightarrow gas is endothermic). Finally, we know that the process takes place without outside intervention, so ΔG is negative.

Think About It

Because ΔG is negative for that process and because ΔH and ΔS are both negative, we can deduce that the enthalpy change for the process is the dominant factor contributing to the spontaneity of the process. We can also see from

$$\Delta G = \Delta H - T\Delta S$$

that the process becomes nonspontaneous at “high” temperature.

12.49. Collect and Organize

For the processes described, we are to determine whether they are spontaneous.

Analyze

Spontaneous processes occur without outside intervention once they are started.

Solve

(a) A tornado forms spontaneously under certain weather conditions.

(b) A broken cell phone does not spontaneously fix itself.

(c) You will not spontaneously get an A in this course.

(d) Hot soup spontaneously cools before being served.

Therefore, (a) and (d) are spontaneous.

Think About It

Spontaneous processes are favored by enthalpy, entropy, or both according to the equation

$$\Delta G = \Delta H - T\Delta S$$

12.50. **Collect and Organize**

For the processes described, we are asked to determine whether they are spontaneous.

Analyze

Spontaneous processes occur without outside intervention once they get started.

Solve

- (a) Wood burns in air once ignited, so that process is spontaneous.
 - (b) Water condenses on a cold glass of iced tea, so that process is spontaneous.
 - (c) Salt dissolves without intervention in water, so that process is spontaneous.
 - (d) Photosynthesis in plants occurs without intervention, so that process is spontaneous.
- Therefore, (a), (b), (c), and (d) are spontaneous.

Think About It

The reverse of all those processes, however, are nonspontaneous.

12.51. **Collect and Organize**

For the dissolution of NaBr and NaI in water, we are to calculate the value of ΔG° knowing the $\Delta H^\circ_{\text{sol}}$ and $\Delta S^\circ_{\text{sol}}$ for both of those soluble salts.

Analyze

We can calculate the value of ΔG° from the standard-state enthalpy and entropy of the reaction by using

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

where $T = 298 \text{ K}$.

Solve

For NaBr:

$$\Delta G^\circ_{\text{rxn}} = -0.60 \text{ kJ/mol} - \left(298 \text{ K} \times \frac{0.057 \text{ kJ}}{\text{mol} \cdot \text{K}} \right) = -18 \text{ kJ/mol}$$

For NaI:

$$\Delta G^\circ_{\text{rxn}} = -7.5 \text{ kJ/mol} - \left(298 \text{ K} \times \frac{0.074 \text{ kJ}}{\text{mol} \cdot \text{K}} \right) = -30 \text{ kJ/mol}$$

Think About It

Be sure to use consistent units for ΔH° and ΔS° in calculations. In this problem, we have to change the ΔS° values given in units of $\text{J/mol} \cdot \text{K}$ to $\text{kJ/mol} \cdot \text{K}$.

12.52. **Collect and Organize**

Given the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ for the reaction of NO with O_2 to give NO_2 , we are to calculate $\Delta G^\circ_{\text{rxn}}$ for the reaction and explain why $\Delta S^\circ_{\text{rxn}}$ is negative for the reaction.

Analyze

We can calculate $\Delta G^\circ_{\text{rxn}}$ from the standard-state enthalpy and entropy of the reaction by using

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

where for that process $\Delta H^\circ_{\text{rxn}} = -12 \text{ kJ}$, $\Delta S^\circ_{\text{rxn}} = -146 \text{ J/K}$ (or -0.146 kJ/K), and $T = 298 \text{ K}$.

Solve

- (a) The value of $\Delta G^\circ_{\text{rxn}}$ from the standard-state enthalpy and entropy of the reaction by using

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= -12 \text{ kJ} - (298 \text{ K} \times -0.146 \text{ kJ/K}) \\ &= 32 \text{ kJ} \end{aligned}$$

- (b) The $\Delta S_{\text{rxn}}^{\circ}$ is negative for that reaction because 3 mol of reactant gases is becoming more ordered (taking up less volume) when forming 2 mol of product.

Think About It

That process is nonspontaneous because the decreasing entropy is dominant. That reaction, however, is spontaneous ($-\Delta G$) at lower temperatures.

12.53. Collect and Organize

For the reaction of C(s) with H₂O(g) to produce H₂(g) and CO(g), we are to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$ from $\Delta G_{\text{f}}^{\circ}$ in Appendix 4.

Analyze

We can calculate $\Delta G_{\text{rxn}}^{\circ}$ by using the values for $\Delta G_{\text{f}}^{\circ}$ for C(s), H₂O(g), H₂(g), and CO(g) in Appendix 4.

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{\text{f,products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^{\circ}$$

Solve

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) + (1 \text{ mol CO} \times -137.2 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) + (1 \text{ mol C} \times 0.0 \text{ kJ/mol}) \right] \\ &= 91.4 \text{ kJ} \end{aligned}$$

Think About It

For that calculation we used carbon in the form of graphite. We would not want to use diamond as a reactant.

12.54. Collect and Organize

For the combustion reaction of 2 mol of methane with 3 mol of oxygen given to produce 2 mol of CO₂ and 4 mol of water vapor, we are to use the appropriate values of $\Delta G_{\text{f}}^{\circ}$ from Appendix 4 to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$.

Analyze

The change in free energy for this reaction is found from G_{f}° values for the reactants and products by using

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{\text{f,products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^{\circ}$$

Solve

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= \left[(2 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) + (4 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) \right] \\ &\quad - \left[(2 \text{ mol CH}_3\text{OH} \times -162.0 \text{ kJ/mol}) + (3 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &= -1379.2 \text{ kJ} \end{aligned}$$

Think About It

That combustion reaction is spontaneous under standard conditions. We might also predict that the change in entropy for that reaction would be positive since 6 mol of product gases is formed from 5 mol of reactant gases.

12.55. Collect and Organize

For the reaction of 1 mol of NO with ½ mol of oxygen given to produce 1 mol of NO₂, we are to use the appropriate values of $\Delta G_{\text{f}}^{\circ}$ from Appendix 4 to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$.

Analyze

The change in free energy for that reaction is found from $\Delta G_{\text{f}}^{\circ}$ values for the reactants and products by using

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{\text{f,products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^{\circ}$$

Solve

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= (1 \text{ mol NO}_2 \times 51.3 \text{ kJ/mol}) - [(1 \text{ mol NO} \times 86.6 \text{ kJ/mol}) + (0.5 \text{ mol O}_2 \times 0.0 \text{ kJ/mol})] \\ &= -35.3 \text{ kJ}\end{aligned}$$

Think About It

That combustion reaction is spontaneous under standard conditions. We might also predict that the change in entropy for that reaction would be negative since 1 mol of product gases is formed from 1.5 mol of reactant gases.

12.56. Collect and Organize

For the decomposition of 2 mol of gaseous ammonia into 1 mol of gaseous nitrogen and 3 mol of gaseous hydrogen, we are to use the appropriate values of ΔG_f° from Appendix 4 to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$.

Analyze

We can use the values in Appendix 4 for ΔG_f° of the products and reactants to calculate $\Delta G_{\text{rxn}}^{\circ}$:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{f,\text{reactants}}^{\circ}$$

Solve

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(1 \text{ mol N}_2 \times 0.0 \text{ kJ/mol}) + (3 \text{ mol H}_2 \times 0.0 \text{ kJ/mol})] \\ &\quad - (2 \text{ mol NH}_3 \times -16.5 \text{ kJ/mol}) \\ &= 33.0 \text{ kJ}\end{aligned}$$

That reaction is not spontaneous at standard conditions.

Think About It

We would predict, however, that the ΔS of that reaction is positive.

12.57. Collect and Organize

For the reaction of 1 mol of gaseous sulfur trioxide with 1 mol of gaseous water to form 1 mol of liquid sulfuric acid, we are to use the appropriate values of ΔG_f° from Appendix 4 to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$.

Analyze

We can use the values in Appendix 4 for ΔG_f° of the products and reactants to calculate $\Delta G_{\text{rxn}}^{\circ}$:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{f,\text{reactants}}^{\circ}$$

Solve

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= (1 \text{ mol H}_2\text{SO}_4 \times -690.0 \text{ kJ/mol}) - [(1 \text{ mol SO}_3 \times -371.1 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol})] \\ &= -90.3 \text{ kJ}\end{aligned}$$

Think About It

Because $\Delta G_{\text{rxn}}^{\circ}$ is negative, that reaction is spontaneous at standard conditions.

12.58. Collect and Organize

For the reaction of 2 mol of gaseous sulfur dioxide with 1 mol of gaseous oxygen to form 2 mol of gaseous sulfur trioxide, we are to use the appropriate values of ΔG_f° from Appendix 4 to calculate the value of $\Delta G_{\text{rxn}}^{\circ}$.

Analyze

We can use the values in Appendix 4 for ΔG_f° of the products and reactants to calculate $\Delta G_{\text{rxn}}^{\circ}$:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{f,\text{reactants}}^{\circ}$$

Solve

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= (2 \text{ mol SO}_3 \times -371.1 \text{ kJ/mol}) - [(2 \text{ mol SO}_2 \times -300.1 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol})] \\ &= -142.0 \text{ kJ}\end{aligned}$$

Think About It

Because $\Delta G_{\text{rxn}}^{\circ}$ is negative, that reaction is spontaneous at standard conditions.

12.59. Collect and Organize

We consider whether exothermic reactions are spontaneous only at low temperature.

Analyze

Spontaneity is shown by a negative free-energy value (ΔG) in the equation

$$\Delta G = \Delta H - T\Delta S$$

For exothermic reactions, we also know that ΔH is negative.

Solve

No. As we can see from the equation, if ΔS is positive, the value of $T\Delta S$ would be positive. Then ΔG would always be negative, regardless of the temperature, and the exothermic reaction would be spontaneous at all temperatures.

Think About It

If ΔS is negative for an exothermic reaction, then it is true that the reaction would be spontaneous only at low temperatures.

12.60. Collect and Organize

We consider whether endothermic reactions can never be spontaneous at low temperatures.

Analyze

Spontaneity is shown by a negative free-energy value (ΔG) in the equation

$$\Delta G = \Delta H - T\Delta S$$

For endothermic reactions, we also know that ΔH is positive.

Solve

As we can see from the equation, for an endothermic reaction to be spontaneous, ΔS must be positive and the temperature must be relatively high. Therefore, yes, endothermic reactions are never spontaneous at low temperature.

Think About It

An endothermic reaction would never be spontaneous, regardless of the temperature, if its ΔS is negative.

12.61. Collect and Organize

For the reaction of C(s) with H₂O(g) to produce H₂(g) and CO(g) in Problem 12.53, we are to predict the lowest temperature at which the reaction is spontaneous.

Analyze

To calculate the lowest temperature at which CO and H₂ form from C and steam, we must first calculate $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ by using Appendix 4. For a spontaneous reaction, ΔG is negative. Therefore, if we set $\Delta G = 0$ and solve for T , that would give the temperature at which the reaction changes spontaneity.

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

We must be sure to have consistent units for ΔH and ΔS for that calculation.

Solve

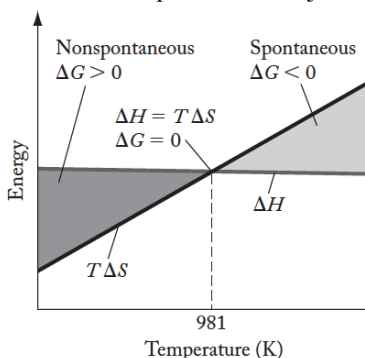
First calculating $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$:

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(1 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) + (1 \text{ mol CO} \times -110.5 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol H}_2\text{O} \times -241.8 \text{ kJ/mol}) + (1 \text{ mol C} \times 0.0 \text{ kJ/mol}) \right] \\ &= 131.3 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= \left[(1 \text{ mol H}_2 \times 130.6 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol CO} \times 197.7 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol C} \times 5.7 \text{ J/mol} \cdot \text{K}) \right] \\ &= 133.8 \text{ J/K}\end{aligned}$$

Solving for T when $\Delta G_{\text{rxn}}^\circ = 0$ gives

$$T = \frac{131.3 \text{ kJ}}{0.1338 \text{ kJ/K}} = 981.3 \text{ K, or } 708.2^\circ\text{C}$$

The lowest temperature at which this reaction is spontaneous is just above 981.3 K, or 708.2°C.

**Think About It**

As in Problem 12.53, we used carbon in the form of graphite to calculate the changes in enthalpy and entropy for the reaction. We would not want to use diamond as a reactant.

12.62. Collect and Organize

For the reaction of 1 mol each of $\text{N}_2(\text{g})$ with $\text{O}_2(\text{g})$ to produce 2 mol of $\text{NO}(\text{g})$, we are to predict the lowest temperature at which the reaction is spontaneous.

Analyze

To calculate the lowest temperature at which NO forms from N_2 and O_2 , we must first calculate $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ by using Appendix 4. For a spontaneous reaction, ΔG is negative. Therefore, if we set $\Delta G = 0$ and solve for T , that would give the temperature at which the reaction changes spontaneity.

$$\begin{aligned}\Delta G = 0 &= \Delta H - T\Delta S \\ T &= \frac{\Delta H}{\Delta S}\end{aligned}$$

We must be sure to have consistent units for ΔH and ΔS for that calculation.

Solve

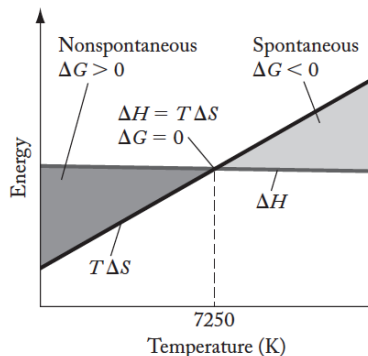
First calculating $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$:

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= (2 \text{ mol NO} \times 90.3 \text{ kJ/mol}) - \left[(1 \text{ mol N}_2 \times 0.0 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &= 180.6 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= (2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) - \left[(1 \text{ mol N}_2 \times 191.5 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\ &= 24.9 \text{ J/K}\end{aligned}$$

Solving for T when $\Delta G_{\text{rxn}}^{\circ} = 0$ gives

$$T = \frac{180.6 \text{ kJ}}{0.0249 \text{ kJ/K}} = 7250 \text{ K, or } 6980^{\circ}\text{C}$$

The lowest temperature at which this reaction is spontaneous is just above 7250 K, or 6980°C.



Think About It

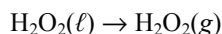
That reaction is not favored by enthalpy but is favored (slightly) by entropy, so at a high enough temperature the reaction will become spontaneous.

12.63. Collect and Organize

For the vaporization of hydrogen peroxide at 1.00 atm, we will first calculate ΔH° and ΔS° . Assuming that calculated quantities (using data listed in Appendix 4 at 298 K) are not temperature dependent, we are to calculate the boiling point of hydrogen peroxide.

Analyze

To calculate both ΔH° and ΔS° for the phase change



we need the following (from Appendix 4): ΔH_f° of $\text{H}_2\text{O}_2(\ell) = -187.8 \text{ kJ/mol}$, ΔH_f° of $\text{H}_2\text{O}_2(\text{g}) = -136.3 \text{ kJ/mol}$, S° of $\text{H}_2\text{O}(\ell) = 109.6 \text{ J/mol} \cdot \text{K}$, and S° of $\text{H}_2\text{O}_2(\text{g}) = 232.7 \text{ J/mol} \cdot \text{K}$. To calculate the boiling point, we can rearrange the Gibbs free-energy equation to solve for the temperature where $\Delta G_{\text{rxn}}^{\circ} = 0$ because at the boiling point $\text{H}_2\text{O}_2(\ell)$ and $\text{H}_2\text{O}_2(\text{g})$ are in equilibrium:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= 0 = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \\ T_b &= \frac{\Delta H_{\text{rxn}}^{\circ}}{\Delta S_{\text{rxn}}^{\circ}}\end{aligned}$$

Solve

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= (1 \text{ mol H}_2\text{O}_2(\text{g}) \times -136.3 \text{ kJ/mol}) - (1 \text{ mol H}_2\text{O}_2(\ell) \times -187.8 \text{ kJ/mol}) \\ &= 51.5 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= (1 \text{ mol H}_2\text{O}_2(\text{g}) \times 232.7 \text{ J/mol} \cdot \text{K}) - (1 \text{ mol H}_2\text{O}_2(\ell) \times 109.6 \text{ J/mol} \cdot \text{K}) \\ &= 123.1 \text{ J/K, or } 0.123 \text{ kJ/K}\end{aligned}$$

$$T_b = \frac{51.5 \text{ kJ}}{0.123 \text{ kJ/K}} = 418 \text{ K, or } 145^{\circ}\text{C}$$

Think About It

Because the calculated value of the boiling point temperature is a little different from the actual T_b (160°C), we can see that some temperature dependence exists for ΔH and ΔS .

12.64. **Collect and Organize**

For the reaction of $\text{SO}_2(\text{g})$ with $\text{H}_2\text{S}(\text{g})$ to form $\text{S}(\text{s})$ and $\text{H}_2\text{O}(\text{g})$, we are to first calculate $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$. Using the Gibbs free-energy equation, we can predict the temperatures over which the reaction is spontaneous.

Analyze

For a reaction to be spontaneous, ΔG must be negative. The temperature at which a reaction changes spontaneity is where $\Delta G_{\text{rxn}}^\circ = 0$. Rearranging the free-energy equation gives

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = 0$$

$$T = \frac{\Delta H_{\text{rxn}}^\circ}{\Delta S_{\text{rxn}}^\circ}$$

Solve

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(3 \text{ mol S} \times 0.0 \text{ kJ/mol}) + (2 \text{ mol H}_2\text{O} \times -241.8 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol SO}_2 \times -296.8 \text{ kJ/mol}) + (2 \text{ mol H}_2\text{S} \times -20.17 \text{ kJ/mol}) \right] \\ &= -146.5 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= \left[(3 \text{ mol S} \times 32.1 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol SO}_2 \times 248.2 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol H}_2\text{S} \times 205.6 \text{ J/mol} \cdot \text{K}) \right] \\ &= -185.5 \text{ J/K} \\ T_b &= \frac{-146.5 \text{ kJ}}{-0.1855 \text{ kJ/K}} = 789.8 \text{ K, or } 516.6^\circ\text{C}\end{aligned}$$

Because that reaction is favored by enthalpy ($-\Delta H$) but not by entropy ($-\Delta S$), it is spontaneous at low temperatures. Therefore, the reaction is spontaneous for temperatures below 789.8 K.

Think About It

The equation specifies that $\text{H}_2\text{O}(\text{g})$ is produced in the reaction, so the useful range for the reaction is 373–789.8 K. Below 373 K, the water is in liquid form.

12.65. **Collect and Organize**

For each reaction we will calculate $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ to determine the sign of each to predict whether each reaction is spontaneous only at low temperatures, only at high temperatures, or at all temperatures.

Analyze

The standard free energy and standard entropy of a reaction can be calculated by using Appendix 4 values for ΔH_f° and ΔS° .

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \sum n \Delta H_{\text{f,products}}^\circ - \sum m \Delta H_{\text{f,reactants}}^\circ \\ \Delta S_{\text{rxn}}^\circ &= \sum n \Delta S_{\text{products}}^\circ - \sum m \Delta S_{\text{reactants}}^\circ\end{aligned}$$

Spontaneity is indicated by a negative free-energy value through the equation

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$$

We can see that an exothermic reaction will be spontaneous at all temperatures if entropy is positive and at low temperatures if entropy is negative. An endothermic reaction will never be spontaneous at any temperature if the entropy is negative but will be spontaneous at high temperature if entropy is positive.

Solve

$$\begin{aligned}\text{(a) } \Delta H_{\text{rxn}}^\circ &= (2 \text{ mol NO}_2 \times 33.2 \text{ kJ/mol}) \\ &\quad - \left[(2 \text{ mol NO} \times 90.3 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &= -114.2 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= (2 \text{ mol NO}_2 \times 240.0 \text{ J/mol} \cdot \text{K}) \\ &\quad - [(2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K})] \\ &= -146.4 \text{ J/K}\end{aligned}$$

Because that reaction is an exothermic reaction with negative entropy, the reaction will be spontaneous (i) only at low temperature.

(b)

Because that reaction is an exothermic reaction with negative entropy, the reaction will be spontaneous (i) only at low temperature.

$$\begin{aligned}\text{(c) } \Delta H_{\text{rxn}}^{\circ} &= [(2 \text{ mol H}_2\text{O} \times -241.8 \text{ kJ/mol}) + (1 \text{ mol N}_2\text{O} \times 82.1 \text{ kJ/mol})] \\ &\quad - (1 \text{ mol NH}_4\text{NO}_3 \times -365.6 \text{ kJ/mol}) \\ &= -35.9 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(2 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol N}_2\text{O} \times 219.9 \text{ J/mol} \cdot \text{K})] \\ &\quad - (1 \text{ mol NH}_4\text{NO}_3 \times 151.1 \text{ J/mol} \cdot \text{K}) \\ &= 446.4 \text{ J/K}\end{aligned}$$

Because that reaction is an exothermic reaction with positive entropy, the reaction will be spontaneous (iii) at all temperatures.

Think About It

For a reaction to be spontaneous only at high temperatures (ii), it would be not favored by enthalpy (endothermic) and would be favored by entropy (positive entropy change).

12.66. Collect and Organize

For each reaction we will calculate $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ to determine the sign of each to predict whether each reaction is spontaneous only at low temperatures, only at high temperatures, or at all temperatures.

Analyze

The standard free energy and standard entropy of a reaction can be calculated by using Appendix 4 values for ΔH_f° and ΔS° .

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \sum n_{\text{products}} \Delta H_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta H_{f,\text{reactants}}^{\circ} \\ \Delta S_{\text{rxn}}^{\circ} &= \sum n_{\text{products}} \Delta S_{\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta S_{\text{reactants}}^{\circ}\end{aligned}$$

Spontaneity is indicated by a negative free-energy value through the equation

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

We can see that an exothermic reaction will be spontaneous at all temperatures if entropy is positive and at low temperatures if entropy is negative. An endothermic reaction will never be spontaneous at any temperature if the entropy is negative but will be spontaneous at high temperature if entropy is positive.

Solve

$$\begin{aligned}\text{(a) } \Delta H_{\text{rxn}}^{\circ} &= (2 \text{ mol MgO} \times -601.6 \text{ kJ/mol}) \\ &\quad - [(2 \text{ mol Mg} \times 0.0 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol})] \\ &= -1203.2 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= (2 \text{ mol MgO} \times 26.95 \text{ J/mol} \cdot \text{K}) \\ &\quad - [(2 \text{ mol Mg} \times 32.7 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K})] \\ &= -216.5 \text{ J/K}\end{aligned}$$

Because that reaction is an exothermic reaction with negative entropy, the reaction will be spontaneous (i) only at low temperature.

$$\begin{aligned}
 \text{(b) } \Delta H_{\text{rxn}}^{\circ} &= \left[(2 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) + (4 \text{ mol H}_2\text{O} \times -285.8 \text{ kJ/mol}) \right] \\
 &\quad - \left[(1 \text{ mol CH}_3\text{OH} \times -238.7 \text{ kJ/mol}) + (3 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\
 &= -169.2 \text{ kJ} \\
 \Delta S_{\text{rxn}}^{\circ} &= \left[(2 \text{ mol CO}_2 \times 213.8 \text{ J/mol} \cdot \text{K}) + (4 \text{ mol H}_2\text{O} \times 69.9 \text{ J/mol} \cdot \text{K}) \right] \\
 &\quad - \left[(1 \text{ mol CH}_3\text{OH} \times 126.8 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\
 &= -34.6 \text{ J/K}
 \end{aligned}$$

Because that reaction is an exothermic reaction with negative entropy, the reaction will be spontaneous (i) only at low temperature.

$$\begin{aligned}
 \text{(c) } \Delta H_{\text{rxn}}^{\circ} &= (2 \text{ mol NO} \times 90.3 \text{ kJ/mol}) \\
 &\quad - \left[(1 \text{ mol N}_2 \times 0.0 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\
 &= 180.6 \text{ kJ} \\
 \Delta S_{\text{rxn}}^{\circ} &= (2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) \\
 &\quad - \left[(1 \text{ mol N}_2 \times 191.5 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol O}_2 \times 205.0 \text{ J/mol} \cdot \text{K}) \right] \\
 &= 24.9 \text{ J/K}
 \end{aligned}$$

Because that reaction is an endothermic reaction with positive entropy, the reaction will be spontaneous (ii) only at high temperature.

Think About It

For a reaction to be spontaneous only at high temperatures (ii), it would be not favored by enthalpy (endothermic) and would be favored by entropy (positive entropy change). For a reaction to be spontaneous at all temperatures, it would have to be favored by both enthalpy (exothermic) and entropy (positive entropy change).

12.67. Collect and Organize

For the reaction of CO with H₂ to produce CH₃OH, we are to use data in Appendix 4 to calculate $\Delta G_{\text{rxn}}^{\circ}$ and then calculate the value of ΔG_{rxn} at 475 K.

Analyze

We can calculate the standard free energy by using Appendix 4 values for ΔG_f° :

$$\Delta G_{\text{rxn}}^{\circ} = \sum n \Delta G_{f,\text{products}}^{\circ} - \sum m \Delta G_{f,\text{reactants}}^{\circ}$$

To determine the value of ΔG_{rxn} at 475 K, we will need to first calculate the values of ΔH° and ΔS° for the reaction through

$$\begin{aligned}
 \Delta H_{\text{rxn}}^{\circ} &= \sum n_{\text{products}} \Delta H_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta H_{f,\text{reactants}}^{\circ} \\
 \Delta S_{\text{rxn}}^{\circ} &= \sum n_{\text{products}} \Delta S_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta S_{f,\text{reactants}}^{\circ}
 \end{aligned}$$

and then apply the equation

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}}$$

If the value of ΔG at 475 K is negative, the reaction is spontaneous.

Solve(a) The value $\Delta G_{\text{rxn}}^\circ$ is

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= (1 \text{ mol CH}_3\text{OH} \times -166.4 \text{ kJ/mol}) \\ &\quad - [(1 \text{ mol CO} \times -137.2 \text{ kJ/mol}) + (2 \text{ mol H}_2 \times 0.0 \text{ kJ/mol})] \\ &= -29.2 \text{ kJ}\end{aligned}$$

That reaction is spontaneous under standard conditions.

(b) $\Delta H_{\text{rxn}}^\circ = (1 \text{ mol CH}_3\text{OH} \times -238.7 \text{ kJ/mol})$

$$\begin{aligned}&\quad - [(1 \text{ mol CO} \times -110.5 \text{ kJ/mol}) + (2 \text{ mol H}_2 \times 0.0 \text{ kJ/mol})] \\ &= -128.2 \text{ kJ}\end{aligned}$$

$$\Delta S_{\text{rxn}}^\circ = (1 \text{ mol CH}_3\text{OH} \times 126.8 \text{ J/mol} \cdot \text{K})$$

$$\begin{aligned}&\quad - [(1 \text{ mol CO} \times 197.7 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol H}_2 \times 130.6 \text{ J/mol} \cdot \text{K})] \\ &= -332.1 \text{ J/K}\end{aligned}$$

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = -128.2 \text{ kJ} - 475 \text{ K}(-0.3321 \text{ kJ/K}) = 29.5 \text{ kJ}$$

That reaction is not spontaneous at 475 K.

Think About It

For that reaction as the temperature is raised, the $T\Delta S$ term in the equation $\Delta G = \Delta H - T\Delta S$ becomes more negative because ΔS for the reaction is negative. That negative term, subtracted from the ΔH value, makes ΔG more positive.

12.68. Collect and Organize

For the reaction of CaO with CO_2 to produce CaCO_3 , we are to use data in Appendix 4 to calculate $\Delta G_{\text{rxn}}^\circ$ and then calculate the value of ΔG_{rxn} at 1500 K to determine the spontaneity of the forward and reverse reactions at that temperature.

Analyze

We can calculate the standard free energy by using Appendix 4 values for ΔG_f° :

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_{f,\text{products}}^\circ - \sum m \Delta G_{f,\text{reactants}}^\circ$$

To determine the value of ΔG_{rxn} at 1500 K, we will need to first calculate the values of ΔH° and ΔS° for the reaction through

$$\Delta H_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta H_{f,\text{products}}^\circ - \sum n_{\text{reactants}} \Delta H_{f,\text{reactants}}^\circ$$

$$\Delta S_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta S_{f,\text{products}}^\circ - \sum n_{\text{reactants}} \Delta S_{f,\text{reactants}}^\circ$$

and then apply the equation

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

If the value of ΔG at 1500 K is negative, the reaction is spontaneous in the forward direction. A reverse reaction has a free energy opposite in sign, but equal in magnitude of the forward reaction.

Solve(a) The value $\Delta G_{\text{rxn}}^\circ$ for this reaction is

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= (1 \text{ mol CaCO}_3 \times -1128.8 \text{ kJ/mol}) \\ &\quad - [(1 \text{ mol CaO} \times -603.3 \text{ kJ/mol}) + (1 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol})] \\ &= -131.1 \text{ kJ}\end{aligned}$$

(b) That reaction is spontaneous at 298 K.

- (c) To calculate free energy at 1500 K, we first need the values of enthalpy and entropy for the reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= (1 \text{ mol CaCO}_3 \times -1206.9 \text{ kJ/mol}) \\ &\quad - \left[(1 \text{ mol CaO} \times -634.9 \text{ kJ/mol}) + (1 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) \right] \\ &= -178.5 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= (1 \text{ mol CaCO}_3 \times 92.9 \text{ J/mol} \cdot \text{K}) \\ &\quad - \left[(1 \text{ mol CaO} \times 38.1 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol CO}_2 \times 213.8 \text{ J/mol} \cdot \text{K}) \right] \\ &= -159.0 \text{ J/K} \\ \Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = -178.5 \text{ kJ} - 1500\text{K}(-0.1590 \text{ kJ/K}) = 60.0 \text{ kJ}\end{aligned}$$

- (d) No, that reaction is not spontaneous at 1500 K.

- (e) Yes, the reverse reaction would be spontaneous at 1500K, with an estimated free energy of -60.0 kJ .

Think About It

For that reaction as the temperature is raised, the $T\Delta S$ term in the equation $\Delta G = \Delta H - T\Delta S$ becomes more negative because ΔS for the reaction is negative. That negative term, subtracted from the ΔH value, makes ΔG more positive.

12.69. Collect and Organize

We are asked to describe how two reactions must complement each other so that a nonspontaneous reaction can be driven by a decrease in free energy of a spontaneous reaction.

Analyze

The overall free energy of the combined reactions must give an overall negative free energy value.

Solve

The spontaneous reaction must have a decrease in free energy that is greater than the increase in free energy for the nonspontaneous reaction.

Think About It

A nonspontaneous process can therefore be coupled to a spontaneous one and thus be “forced” to go.

12.70. Collect and Organize

We are to express how to calculate the free energy of a reaction that couples two other reactions, one spontaneous and the other nonspontaneous.

Analyze

When coupling reactions, we can add the free energy of each reaction because free energy is a state function, just like enthalpy and entropy.

Solve

To obtain the free energy of the overall reaction for the coupling of two reactions, we add the free energies.

Think About It

If the free energy of the spontaneous reaction is more negative than the free energy of the nonspontaneous reaction, then the overall coupled reaction will be spontaneous.

12.71. Collect and Organize

We are to explain the importance of why some steps in glycolysis to form ATP from ADP are spontaneous.

Analyze

A reaction that is spontaneous has a negative value for its free energy change.

Solve

ATP has the important function of energy storage and transfer. The cell must make that important molecule and so the overall process must be spontaneous. Even if some of the glycolysis steps are nonspontaneous, at least some glycolysis steps must be spontaneous to produce ATP.

Think About It

In Figure 12.22, the only difference between ADP and ATP is the presence of an additional phosphate group in ATP.

12.72. Collect and Organize

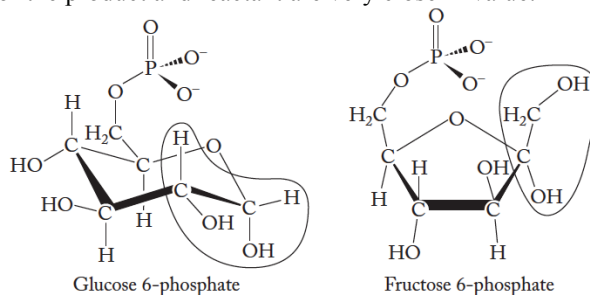
By examining the structures of glucose 6-phosphate and fructose 6-phosphate in Figure P12.72, we can explain why the conversion between these two sugars has a ΔG° close to zero.

Analyze

Changes in free energy result from changes in enthalpy (related to the number and types of chemical bonds) and changes in entropy (disorder in the system).

Solve

In the conversion of glucose 6-phosphate to fructose 6-phosphate, the six-membered ring becomes a five-membered ring. The bond arrangements are only slightly different between the two structures, and so the enthalpies and entropies of the product and reactant are very close in value.

**Think About It**

Glucose 6-phosphate and fructose 6-phosphate are structural isomers of each other.

12.73. Collect and Organize

Here we explore the free energy of the steps used in the steam–methane reforming process to produce hydrogen from methane.

Analyze

We will use the values for ΔG_f° in Appendix 4 for the reactant and products to determine the free energy for the reaction of methane with water and for carbon monoxide with water. The free energy of each reaction can be calculated using

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_{f,\text{products}}^\circ - \sum m \Delta G_{f,\text{reactants}}^\circ$$

Then we will couple the two reactions to calculate the $\Delta G_{\text{rxn}}^\circ$ for the overall process and predict whether it is spontaneous under standard conditions.

Solve

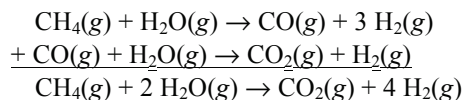
- (a) For the reaction of 1 mol of methane with 1 mol of water to form 1 mol of carbon monoxide and 3 mol of hydrogen:

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \left[(1 \text{ mol CO} \times -137.2 \text{ kJ/mol}) + (3 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol CH}_4 \times -50.8 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) \right] \\ &= 142.2 \text{ kJ} \end{aligned}$$

- (b) For the reaction of 1 mol of carbon monoxide with 1 mol of water to form 1 mol of carbon dioxide and 1 mol of hydrogen:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) + (1 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol CO} \times -137.2 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) \right] \\ &= -28.6 \text{ kJ}\end{aligned}$$

- (c) Adding those reactions:



- (d) $\Delta G_{\text{overall}}^{\circ} = 142.2 + (-28.6) = 113.6 \text{ kJ}$. That reaction is not spontaneous at standard conditions.

Think About It

If the temperature is raised, however, the reaction does become spontaneous.

12.74. Collect and Organize

Here we explore the free energy of the decomposition of methane to carbon and subsequent reaction of the carbon with oxygen along with the coupled reaction of the two processes.

Analyze

We will use the values for ΔG_f° in Appendix 4 for the reactant and products to determine the free energy for the decomposition reaction of methane and for carbon with oxygen. The free energy of each reaction can be calculated by using

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{f,\text{reactants}}^{\circ}$$

Then we will couple the two reactions to calculate the $\Delta G_{\text{rxn}}^{\circ}$ for the overall process and predict whether it is spontaneous under standard conditions.

Solve

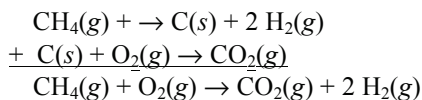
- (a) For the decomposition of 1 mol of methane to form 1 mol of carbon and 2 mol of hydrogen:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol C} \times 0.0 \text{ kJ/mol}) + (3 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol CH}_4 \times -50.8 \text{ kJ/mol}) \\ &= 50.8 \text{ kJ}\end{aligned}$$

For the reaction of 1 mol of carbon with 1 mol of oxygen to form 1 mol of carbon dioxide:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= (1 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) \\ &\quad - \left[(1 \text{ mol C} \times 0.0 \text{ kJ/mol}) + (1 \text{ mol O}_2 \times 0.0 \text{ kJ/mol}) \right] \\ &= -394.4 \text{ kJ}\end{aligned}$$

- (b) Adding those reactions:



$$\Delta G_{\text{overall}}^{\circ} = 50.8 + (-394.4) = -343.6 \text{ kJ}. \text{ The reaction is spontaneous at standard conditions.}$$

Think About It

The enthalpy change for the overall reaction at standard conditions is -338.1 kJ and the entropy change for reaction at standard conditions is -139.3 J/K . That indicates that the reaction is favored by enthalpy and not by entropy, and so the reaction will become nonspontaneous at high temperatures.

12.75. Collect and Organize

We are asked to calculate the free energy for the reaction between Fe_2O_3 and CO to form Fe and CO_2 at 1450°C .

Analyze

To determine the value of ΔG_{rxn} at 1450°C (1723 K), we will need to first calculate the values of ΔH° and ΔS° for the reaction through

$$\Delta H_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta H_{\text{f,products}}^\circ - \sum n_{\text{reactants}} \Delta H_{\text{f,reactants}}^\circ$$

$$\Delta S_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta S_{\text{products}}^\circ - \sum n_{\text{reactants}} \Delta S_{\text{reactants}}^\circ$$

and then apply the equation with $T = 1723 \text{ K}$.

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

Solve

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(2 \text{ mol Fe} \times 0.0 \text{ kJ/mol}) + (3 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol Fe}_2\text{O}_3 \times -824.2 \text{ kJ/mol}) + (3 \text{ mol CO} \times -110.5 \text{ kJ/mol}) \right] \\ &= -24.8 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= \left[(2 \text{ mol Fe} \times 27.3 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol CO}_2 \times 213.8 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol Fe}_2\text{O}_3 \times 87.4 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol CO} \times 197.7 \text{ J/mol} \cdot \text{K}) \right] \\ &= 15.5 \text{ J/K} \\ \Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = -24.8 \text{ kJ} - 1723\text{K}(0.0155 \text{ kJ/K}) = -51.5 \text{ kJ}\end{aligned}$$

Think About It

The reaction is spontaneous at that temperature, as indicated by the negative value of the free energy.

12.76. Collect and Organize

We are asked to calculate the free energy for the reaction between Fe_2O_3 and C (coke, a form of carbon with the thermodynamic properties of graphite) to form Fe and CO_2 at 1450°C .

Analyze

First we will have to write a balanced chemical equation for the reaction:



To determine the value of ΔG_{rxn} at 1450°C (1723 K), we will need to first calculate the values of ΔH° and ΔS° for the reaction through

$$\Delta H_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta H_{\text{f,products}}^\circ - \sum n_{\text{reactants}} \Delta H_{\text{f,reactants}}^\circ$$

$$\Delta S_{\text{rxn}}^\circ = \sum n_{\text{products}} \Delta S_{\text{products}}^\circ - \sum n_{\text{reactants}} \Delta S_{\text{reactants}}^\circ$$

and then apply the equation with $T = 1723 \text{ K}$.

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

The value we calculate will be for the reduction of 2 mol of Fe_2O_3 . To compare the free energy for that reaction to that in Problem 12.75, we will have to divide the result by 2.

Solve

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(4 \text{ mol Fe} \times 0.0 \text{ kJ/mol}) + (3 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) \right] \\ &\quad - \left[(2 \text{ mol Fe}_2\text{O}_3 \times -824.2 \text{ kJ/mol}) + (3 \text{ mol C} \times 0.0 \text{ kJ/mol}) \right] \\ &= 467.9 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= \left[(4 \text{ mol Fe} \times 27.3 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol CO}_2 \times 213.8 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(2 \text{ mol Fe}_2\text{O}_3 \times 87.4 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol C} \times 5.7 \text{ J/mol} \cdot \text{K}) \right] \\ &= 558.7 \text{ J/K} \\ \Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} = 467.9 \text{ kJ} - 1723\text{K}(0.5587 \text{ kJ/K}) = -49.5 \text{ kJ}\end{aligned}$$

For 1 mol of Fe_2O_3 reduced, the free energy is

$$\frac{-49.5 \text{ kJ}}{2 \text{ mol}} = -24.7 \text{ kJ/mol Fe}_2\text{O}_3$$

Think About It

The reaction is spontaneous at that temperature, as indicated by the negative value of the free energy, but is slightly less spontaneous than the reaction using carbon monoxide (Problem 12.75).

12.77. Collect and Organize

Given the boiling point (23.8°C) and molar heat of vaporization (24.8 kJ/mol) of trichlorofluoromethane, we are to calculate the molar entropy of evaporation of that liquid.

Analyze

Because phase changes are isothermal processes (meaning they take place at constant temperature),

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

We also know that $q_{\text{rev}} = \Delta H_{\text{rxn}}$, so

$$\Delta S_{\text{rxn}} = \frac{\Delta H_{\text{rxn}}}{T_b}$$

where ΔH_{rxn} is the enthalpy of the phase change and T is the temperature at which the phase change occurs, expressed in kelvin.

Solve

$$\Delta S = \frac{24.8 \text{ kJ/mol}}{296.95 \text{ K}} = 8.35 \times 10^{-2} \text{ kJ/mol} \cdot \text{K}, \text{ or } 83.5 \text{ J/mol} \cdot \text{K}$$

Think About It

The positive entropy change makes sense because in vaporizing the chlorofluorocarbon, we are increasing the entropy of the system.

12.78. Collect and Organize

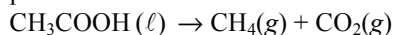
We can determine $\Delta H_{\text{rxn}}^\circ$ and $\Delta G_{\text{rxn}}^\circ$ for the conversion of acetic acid to CO_2 and CH_4 to answer whether the reaction is exothermic and spontaneous under standard conditions.

Analyze

We can use the standard molar enthalpies and molar free energies in Appendix 4 to calculate the enthalpy and free energy change for the reaction.

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \sum n_{\text{products}} H_{\text{f,products}}^\circ - \sum n_{\text{reactants}} H_{\text{f,reactants}}^\circ \\ \Delta G_{\text{rxn}}^\circ &= \sum n_{\text{products}} \Delta G_{\text{f,products}}^\circ - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^\circ\end{aligned}$$

We first need, however, to write the equation and make sure that it is balanced.



Solve

(a) With positive ΔH , that reaction is endothermic.

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(1 \text{ mol CH}_4 \times -74.8 \text{ kJ/mol}) + (1 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol CH}_3\text{COOH} \times -484.5 \text{ kJ/mol}) \\ &= 16.2 \text{ kJ}\end{aligned}$$

(b) Yes, that reaction is spontaneous under standard conditions.

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol CH}_4 \times -50.8 \text{ kJ/mol}) + (1 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol CH}_3\text{COOH} \times -389.9 \text{ kJ/mol}) \\ &= -55.3 \text{ kJ}\end{aligned}$$

Think About It

The ΔS must be positive for that reaction to be endothermic but spontaneous.

12.79. Collect and Organize

For the decomposition of solid NH_4Cl into gaseous NH_3 and HCl , we are to calculate the temperature at which $\Delta G_{\text{rxn}}^{\circ} = 0$.

Analyze

To answer that, we need to first calculate $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ by using values in Appendix 4. Then we can calculate T by rearranging the free-energy equation:

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = 0 \\ T &= \frac{\Delta H_{\text{rxn}}^{\circ}}{\Delta S_{\text{rxn}}^{\circ}}\end{aligned}$$

Solve

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol NH}_3 \times -46.1 \text{ kJ/mol}) + (1 \text{ mol HCl} \times -92.3 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol NH}_4\text{Cl} \times -314.4 \text{ kJ/mol}) \\ &= 176.0 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol NH}_3 \times 192.5 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol HCl} \times 186.9 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - (1 \text{ mol NH}_4\text{Cl} \times 94.6 \text{ J/mol} \cdot \text{K}) \\ &= 284.8 \text{ J/K} \\ T &= \frac{176.0 \text{ kJ}}{0.2848 \text{ kJ/K}} = 618.0 \text{ K, or } 344.8^{\circ}\text{C}\end{aligned}$$

Think About It

The reaction is favored by entropy but not by enthalpy. It is spontaneous at high temperature.

12.80. Collect and Organize

For the precipitation of magnesium hydroxide and silver chloride, we are to compare our prediction for the sign of the entropy change for each precipitation reaction with that of the calculated values.

Analyze

Entropy for a process generally decreases when the number of independent particles in a process decreases. We calculate the entropy change for each precipitation reaction by using

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_{\text{products}} S_{\text{products}}^{\circ} - \sum n_{\text{reactants}} S_{\text{reactants}}^{\circ}$$

and the values from Appendix 4 for the reactants and products for each precipitation.

Solve

(a) Because the precipitation process results in fewer particles from reactants to products, we predict that the sign of $\Delta S_{\text{rxn}}^{\circ}$ will be negative for both reactions.

(b) For the precipitation of $\text{Mg}(\text{OH})_2$, the change in entropy is

$$\Delta S_{\text{rxn}}^{\circ} = (1 \text{ mol Mg}(\text{OH})_2 \times 63.2 \text{ J/mol} \cdot \text{K}) - \left[(1 \text{ mol Mg}^{2+} \times -138.1 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol OH}^{-} \times -10.8 \text{ J/mol} \cdot \text{K}) \right] \\ = 222.9 \text{ J/K}$$

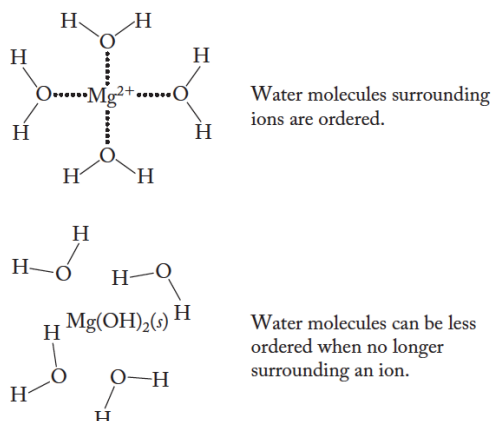
For the precipitation of AgCl , the change in entropy is

$$\Delta S_{\text{rxn}}^{\circ} = (1 \text{ mol AgCl} \times 96.2 \text{ J/mol} \cdot \text{K}) - \left[(1 \text{ mol Ag}^{+} \times 72.7 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol Cl}^{-} \times 56.5 \text{ J/mol} \cdot \text{K}) \right] \\ = -33.0 \text{ J/K}$$

(c) Only for the precipitation of silver chloride was the prediction correct.

Think About It

The predictions we made for those precipitation reactions ignored the entropy change of the water that is initially coordinated to the ions when the water molecules are released back into the bulk water solution upon precipitation.



12.81. Collect and Organize

For the gas-phase reaction of NO with H_2 to form N_2 and H_2O , we can use the values of ΔG_f° in Appendix 4 to calculate $\Delta G_{\text{rxn}}^{\circ}$ and then determine whether the reaction is spontaneous.

Analyze

We can use the values for ΔG_f° of the products and reactants to calculate $\Delta G_{\text{rxn}}^{\circ}$:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{f,\text{products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{f,\text{reactants}}^{\circ}$$

If $\Delta G_{\text{rxn}}^{\circ}$ is negative, then the reaction is spontaneous.

Solve

$$\Delta G_{\text{rxn}}^{\circ} = \left[(1 \text{ mol N}_2 \times 0.0 \text{ kJ/mol}) + (2 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) \right] \\ - \left[(2 \text{ mol NO} \times 86.6 \text{ kJ/mol}) + (2 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) \right] \\ = -630.4 \text{ kJ}$$

Yes, the reaction is spontaneous at standard temperature and pressure.

Think About It

Because 4 mol of gas combines as reactants and forms 3 mol of gas as products, we predict that $\Delta S_{\text{rxn}}^{\circ}$ is negative. From the data in Appendix 4, we see that this is indeed the case:

$$\Delta S_{\text{rxn}}^{\circ} = \left[(1 \text{ mol N}_2 \times 191.5 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) \right] \\ - \left[(2 \text{ mol NO} \times 210.7 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol H}_2 \times 130.6 \text{ J/mol} \cdot \text{K}) \right] \\ = -113.5 \text{ J/K}$$

12.82. Collect and Organize

We are to explain Rudolf Clausius's statement on the second law of thermodynamics in light of concepts learned in this chapter.

Analyze

Clausius's statement on the second law of thermodynamics here emphasizes the summation of entropy for a system.

Solve

You answer may vary. Entropy, a state function that can be summed for a cyclical process, will show an increase because the overall entropy change ($\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$) will increase for an irreversible process. For a reversible process, which is rarer, the entropy change is zero.

Think About It

Recall that a reversible process is one in which such a small change has been made that the system is restored to the original state of the system with no energy flow.

12.83. Collect and Organize

For HCN we are to calculate the normal boiling point (T_b) given ΔH_f° and S° values for $\text{HCN}(\ell)$ and $\text{HCN}(g)$.

Analyze

At the boiling point, $\Delta G = 0$ because the system is at equilibrium. Therefore,

$$\Delta G = 0 = \Delta H_{\text{vap}}^\circ - T_b \Delta S_{\text{vap}}^\circ$$

$$T = \frac{\Delta H_{\text{vap}}^\circ}{\Delta S_{\text{vap}}^\circ}$$

Solve

For the vaporization process

$$\text{HCN}(\ell) \rightarrow \text{HCN}(g)$$

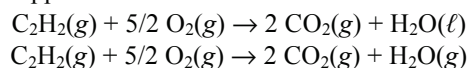
$$\begin{aligned}\Delta H_{\text{vap}} &= (1 \text{ mol HCN}(g) \times 135.1 \text{ kJ/mol}) - (1 \text{ mol HCN}(\ell) \times 108.9 \text{ kJ/mol}) \\ &= 26.2 \text{ kJ} \\ \Delta S_{\text{vap}} &= (1 \text{ mol HCN}(g) \times 202 \text{ J/mol} \cdot \text{K}) - (1 \text{ mol HCN}(\ell) \times 113 \text{ J/mol} \cdot \text{K}) \\ &= 89 \text{ J/K} \\ T_b &= \frac{26.2 \text{ kJ}}{0.089 \text{ kJ/K}} = 294 \text{ K}\end{aligned}$$

Think About It

The actual boiling point of $\text{HCN}(\ell)$ is 299 K, just about room temperature, so our calculation is approximately correct.

12.84. Collect and Organize

We are asked to use ΔG_f° values in Appendix 4 to estimate the ΔG at 298 K for the reactions



Then we will comment on how we might determine the difference between those two free-energy values without specifically solving for $\Delta G_{\text{rxn}}^\circ$.

Analyze

We can use the values for ΔG_f° of the products and reactants to calculate $\Delta G_{\text{rxn}}^\circ$:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_{\text{products}} \Delta G_{\text{f,products}}^{\circ} - \sum n_{\text{reactants}} \Delta G_{\text{f,reactants}}^{\circ}$$

In examining the difference in free energy between the reactions, we will consider qualitatively the difference in free energy of gaseous versus liquid water and how that affects the free energy calculation for the reactions.

Solve

(a) For the reaction in which liquid water is formed:

$$\begin{aligned} \text{C}_2\text{H}_2(g) + 5/2 \text{O}_2(g) &\rightarrow 2 \text{CO}_2(g) + \text{H}_2\text{O}(\ell) \\ \Delta G_{\text{rxn}}^{\circ} &= \left[(2 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O} \times -237.2 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol C}_2\text{H}_2 \times 209.2 \text{ kJ/mol}) + \left(\frac{5}{2} \text{ mol O}_2 \times 0.0 \text{ kJ/mol} \right) \right] \\ &= -1235.2 \text{ kJ} \end{aligned}$$

(b) For the reaction in which gaseous water is formed:

$$\begin{aligned} \text{C}_2\text{H}_2(g) + 5/2 \text{O}_2(g) &\rightarrow 2 \text{CO}_2(g) + \text{H}_2\text{O}(g) \\ \Delta G_{\text{rxn}}^{\circ} &= \left[(2 \text{ mol CO}_2 \times -394.4 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O} \times -228.6 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol C}_2\text{H}_2 \times 209.2 \text{ kJ/mol}) + \left(\frac{5}{2} \text{ mol O}_2 \times 0.0 \text{ kJ/mol} \right) \right] \\ &= -1226.4 \text{ kJ} \end{aligned}$$

(c) The free energy of formation of liquid water is more negative than that of gaseous water (by 8.6 kJ/mol). Because water is a product in the reactions, the free energy for the reaction that produces liquid water will be more negative than the reaction that produces gaseous water as a result.

Think About It

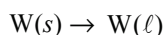
The more negative free energy of liquid water is due to the more negative enthalpy of formation of liquid water (−285.8 kJ/mol) than that of gaseous water (−241.8 kJ/mol).

12.85. Collect and Organize

Given the melting point T_m (3422°C) and ΔH_{fus} (35.4 kJ/mol) of tungsten, we are to calculate ΔS_{fus} .

Analyze

The reaction for that process is



At the melting point, $\Delta G = 0$ because the system is at equilibrium. Therefore,

$$\begin{aligned} \Delta G = 0 &= \Delta H_{\text{fus}} - T_m \Delta S_{\text{fus}} \\ \Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{T_m} \end{aligned}$$

Solve

$$\Delta S_{\text{fus}} = \frac{35.4 \text{ kJ/mol}}{3695 \text{ K}} = 0.00958 \text{ kJ/mol} \cdot \text{K}, \text{ or } 9.58 \text{ J/mol} \cdot \text{K}$$

Think About It

Tungsten has the highest melting point of all the metals, making it useful as a filament in incandescent lightbulbs.

12.86. Collect and Organize

We are asked to calculate the absolute molar entropy for silicon with different numbers of probable arrangements of the silicon atoms.

Analyze

To calculate absolute entropy, S , we use Boltzmann's equation

$$S = k_B \ln W$$

where $k_B = 1.381 \times 10^{-23} \text{ J/K}$.

Solve

(a) When $W = 16$

$$S = k_B \ln W = 1.381 \times 10^{-23} \text{ J/K} \ln(16) = 3.829 \times 10^{-23} \text{ J/K}$$

$$\text{For 1 mol of silicon} = 3.829 \times 10^{-23} \text{ J/K} \times 6.022 \times 10^{23} / \text{mol} = 23 \text{ J/K} \cdot \text{mol}$$

(b) When $W = 625$

$$S = k_B \ln W = 1.381 \times 10^{-23} \text{ J/K} \ln(625) = 8.890 \times 10^{-23} \text{ J/K}$$

$$\text{For 1 mol of silicon} = 8.890 \times 10^{-23} \text{ J/K} \times 6.022 \times 10^{23} / \text{mol} = 53.5 \text{ J/K} \cdot \text{mol}$$

(c) When $W = 2500$

$$S = k_B \ln W = 1.381 \times 10^{-23} \text{ J/K} \ln(2500) = 1.080 \times 10^{-22} \text{ J/K}$$

$$\text{For 1 mol of silicon} = 1.080 \times 10^{-22} \text{ J/K} \times 6.022 \times 10^{23} / \text{mol} = 65 \text{ J/K} \cdot \text{mol}$$

Think About It

As the number of probable arrangements increases, the absolute entropy increases.

12.87. Collect and Organize

Given the transition temperature (369 K) and the enthalpy change for the interconversion of two allotropes of S_8 (297 J/mol), we are to calculate the entropy change for the transition.

Analyze

At the transition temperature, $\Delta G = 0$ because the system is at equilibrium. Therefore,

$$\Delta G = 0 = \Delta H_{\text{trans}} - T \Delta S_{\text{trans}}$$

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T}$$

Solve

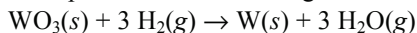
$$\Delta S_{\text{trans}} = \frac{297 \text{ J/mol}}{369 \text{ K}} = 0.805 \text{ J/mol} \cdot \text{K}$$

Think About It

That transition, not favored by enthalpy (ΔH positive), is favored by entropy (ΔS positive).

12.88. Collect and Organize

We are asked to determine over which temperatures the following reaction is spontaneous:

**Analyze**

First, we have to determine $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ by using values in Appendix 4 for $\text{H}_2(g)$ and $\text{H}_2\text{O}(g)$. We are given the standard enthalpy of formation of WO_3 (-843 kJ/mol) and its standard molar entropy ($76 \text{ J/mol} \cdot \text{K}$). The molar entropy of $\text{W}(s)$ is also given in Appendix 4 as $32.6 \text{ J/mol} \cdot \text{K}$, with the enthalpy of formation of the element equal to 0.0 kJ/mol , by definition. Then we calculate T from the free-energy equation:

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 0$$

$$T = \frac{\Delta H_{\text{rxn}}^\circ}{\Delta S_{\text{rxn}}^\circ}$$

Solve

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \left[(1 \text{ mol W} \times 0.0 \text{ kJ/mol}) + (3 \text{ mol H}_2\text{O} \times -241.8 \text{ kJ/mol}) \right] \\ &\quad - \left[(1 \text{ mol WO}_3 \times -843 \text{ kJ/mol}) + (3 \text{ mol H}_2 \times 0.0 \text{ kJ/mol}) \right] = 117.6 \text{ kJ} \end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol W} \times 32.6 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol H}_2\text{O} \times 188.8 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - \left[(1 \text{ mol WO}_3 \times 76 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol H}_2 \times 130.6 \text{ J/mol} \cdot \text{K}) \right] = 131.2 \text{ J/K} \\ T &= \frac{117.6 \text{ kJ}}{0.1312 \text{ kJ/K}} = 896 \text{ K}\end{aligned}$$

That reaction is spontaneous at temperatures higher than 896 K, or 623°C.

Think About It

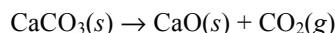
Be careful to use the appropriate values for the phases of the reactants and products. In this problem, the water is gaseous.

12.89. Collect and Organize

Using the values given for ΔH_f° and S° for CaCO_3 , CaO , and CO_2 , we are to explain why S° of CaCO_3 is higher than that of CaO and calculate the temperature at which the pressure of CO_2 over CaCO_3 is 1.0 atm.

Analyze

By considering the phase and size of each compound, we can rank the compounds in order of increasing standard molar entropy. The reaction involved is



To calculate the temperature at which the partial pressure of CO_2 is 1.0 atm, we must recognize that at that temperature the reaction will be at equilibrium, $\Delta G = 0$.

Solve

S° for CaCO_3 is greater than S° for CaO because more atoms are in CaCO_3 .

To calculate the temperature at which the pressure of CO_2 is 1.0 atm, we must first calculate $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol CaO} \times -636 \text{ kJ/mol}) + (1 \text{ mol CO}_2 \times -394 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol CaCO}_3 \times -1207 \text{ kJ/mol}) \\ &= 177 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= \left[(1 \text{ mol CaO} \times 40 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol CO}_2 \times 214 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - (1 \text{ mol CaCO}_3 \times 93 \text{ J/mol} \cdot \text{K}) \\ &= 161 \text{ J/K} \\ \Delta G = 0 &= 177 \text{ kJ} - T \times 0.161 \text{ kJ/K} \\ T &= 1099 \text{ K, or } 826^{\circ}\text{C}\end{aligned}$$

Think About It

Although that reaction is endothermic, it is favored by entropy and so is spontaneous at high temperature.

12.90. Collect and Organize

In considering the conversion of Cu_2O to CuO , we are to name the oxides of copper in that reaction, compare the standard molar entropies of the oxides, and calculate the temperatures at which the reaction is spontaneous.

Analyze

- To name the oxides, we have to determine the oxidation states of the copper in each compound to specify the Roman numeral needed in the compound name. The oxide ion has a 2− charge.
- To predict the range of temperatures over which the reaction is spontaneous, we will have to compute $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ and then use the Gibbs free-energy equation to solve for T when $\Delta G_{\text{rxn}} = 0$:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = 0 \\ T &= \frac{\Delta H_{\text{rxn}}^{\circ}}{\Delta S_{\text{rxn}}^{\circ}}\end{aligned}$$

(c) In considering why S° is larger for Cu_2O than for CuO , we can look at the complexity of the two molecules.

Solve

(a) Cu_2O is copper(I) oxide and CuO is copper(II) oxide.

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[(1 \text{ mol CuO} \times -156.1 \text{ kJ/mol}) + (1 \text{ mol Cu} \times 0.0 \text{ kJ/mol}) \right] \\ &\quad - (1 \text{ mol Cu}_2\text{O} \times -170.7 \text{ kJ/mol}) = 14.6 \text{ kJ} \\ \Delta S_{\text{rxn}}^\circ &= \left[(1 \text{ mol CuO} \times 42.6 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol Cu} \times 33.2 \text{ J/mol} \cdot \text{K}) \right] \\ &\quad - (1 \text{ mol Cu}_2\text{O} \times 92.4 \text{ J/mol} \cdot \text{K}) = -16.6 \text{ J/K} \\ T &= \frac{14.6 \text{ kJ}}{-0.0166 \text{ kJ/K}} = -880 \text{ K}\end{aligned}$$

That would give a negative temperature in kelvin, which is impossible. That reaction is never spontaneous over any range of temperature.

(c) Cu_2O is more complex than CuO because it has more bonds; therefore, Cu_2O has greater molar entropy.

Think About It

The reverse reaction, the production of Cu_2O from CuO and Cu , would be spontaneous at all temperatures.

12.91. Collect and Organize

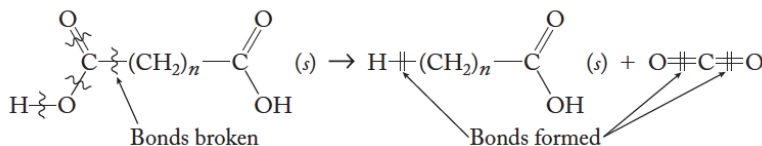
For the process in which a linear chain dicarboxylic acid decomposes to CO_2 and an alkylcarboxylic acid, we are asked to predict the sign of ΔH and ΔS . We are also to predict the spontaneity for the reverse reaction.

Analyze

(a) To predict the signs of ΔH and ΔS , we should recall that breaking bonds takes energy, but energy is released when bonds are formed; also, the generation of gaseous products from a solid or liquid reactant increases the disorder of the system.

Solve

(a) We can estimate the enthalpy of reaction by using the bond energy values in Table 4.6 in the textbook. In the reaction, 1 mol of C—C bonds (between one carboxylic acid group and the alkyl chain), 1 mol of C—O bonds, 1 mol of C=O bonds, and 1 mol of O—H bonds (all from the carboxylic acid group) are broken, whereas 1 mol of C—H bonds and 2 mol of C=O bonds (in CO_2) are formed.



Using the bond energy values, we get an enthalpy of reaction of

$$\begin{aligned}\Delta H &= \left[(1 \times 348 \text{ kJ/mol}) + (1 \times 358 \text{ kJ/mol}) + (1 \times 743 \text{ kJ/mol}) + (1 \times 463 \text{ kJ/mol}) \right] \\ &\quad + \left[(1 \times -413 \text{ kJ/mol}) + (2 \times -799 \text{ kJ/mol}) \right] \\ &= -99 \text{ kJ}\end{aligned}$$

The sign of ΔH is negative, and the reaction is exothermic.

Because a gaseous product (CO_2) is formed in that reaction, ΔS is positive.

(b) The reverse reaction would have $+\Delta H$ and $-\Delta S$ and, therefore, would never be spontaneous.

Think About It

The forward reaction, being favored by both entropy and enthalpy, is spontaneous at all temperatures.

12.92. **Collect and Organize**

We consider what changes occur in ΔS for the heating and cooling of DNA, and then we are to write an equation that relates the melting temperature of DNA to ΔH and ΔS .

Analyze

(a and b) Entropy is a measure of disorder in the system. As DNA unwinds into its two single strands, more disorder is present in the system.

(c) At the melting point, $\Delta G = 0$. We can rearrange the free-energy equation

$$\Delta G = \Delta H - T\Delta S = 0$$

to solve for T .

Solve

(a) The sign of ΔS for the process of DNA separating into two strands through heating is positive.

(b) ΔS for the re-formation of the double helix of DNA is negative.

(c) $\Delta H - T\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S}$$

Think About It

When $\Delta G = 0$, the system is at equilibrium, as we will see in the study of chemical equilibria in Chapter 16.